Determinations of Atomic Weights.

Further Investigation Concerning the Atomic Weights of Silver, Lithium and Chlorine.

By Theodore W. Richards and Hobart Hurd Willard.

The Harvard Determinations of Atomic Weights, between 1870 and 1910.

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Methods Used in Precise Chemical Investigation.

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CARNEGIE INSTITUTION OF WASHINGTON
PUBLICATION No. 125

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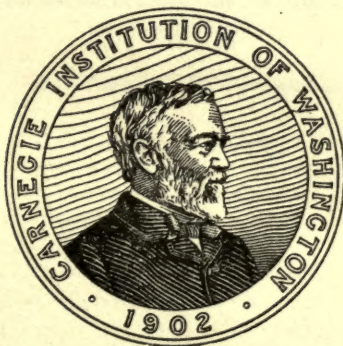
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PART I.

THE RATIO OF LITHIUM CHLORIDE TO SILVER CHLORIDE AND SILVER.[1]

INTRODUCTION.

The present uncertainty in the atomic weight of silver causes confusion and uncertainty throughout the whole table of atomic weights. Long ago Dumas[2] pointed out that Stas, with all his care, had not succeeded in preparing pure silver, and accordingly that the atomic weights referred to silver need revision. Later, in reply to Dumas, Stas[3] sought to determine the oxygen remaining in the metal and succeeded in finding only a trace. Hence for many years Dumas's criticism was unheeded. A careful study of Stas's experiments shows, however, that the metal which he used in these later trials had not been treated in the same way as that which he used in his work upon atomic weights and hence that the presence or absence of oxygen in the later samples proved little with regard to the earlier samples. As a matter of fact, it was shown in 1903, in the chemical laboratory of Harvard University,[4] that Stas's silver must have been impure to the extent of at least 0.015 per cent and that therefore his value for the atomic weight of this element, as well as of the others which had been referred to it, must have been in error. Clearly Stas's value for silver must be too large, but no attempt was made at that time to discover just how great the error might be, this proof being a somewhat complicated matter. Since that time increasing evidence has been presented, especially by Guye, tending to show that the discrepancy is serious. Because most other elements are referred to oxygen only through silver, on account of the insolubility of many silver salts and their consequent ease of precipitation, this uncertainty in the atomic weight of silver is of very serious moment. Indeed a majority of the atomic weights can not be referred to oxygen with precision until the relation between silver and oxygen is ascertained without doubt.[5]

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[1] This paper is also published in Journ. Amer. Chem. Soc., 32, 4 (1910).
[2] Dumas, Ann. chim. phys., 14, 289 (1878).
[3] Stas, Oeuvres Complètes, III, 106–125 (Brussels, 1903).
[4] Richards and Wells, A Revision of the Atomic Weights of Sodium and Chlorine. Carnegie Institution of Washington Publication No. 28; Journ. Amer. Chem. Soc., 27, 459 (1905); Z. anorg. Chem., 47, 56 (1905). This paper is reprinted in full in "Experimentelle Untersuchungen über die Atomgewichte," by T. W. Richards, p. 689 (Hamburg, 1909), and also in Chem. News, vol. 93.
[5] Report International Committee on Atomic Weights, 1906; Guye and Ter Gazarian, Compt. rend., 143, 411 (1906); Noyes, Journ. Amer. Chem. Soc., 29, 1717 (1907).

To discover the most suitable method of attaining this end and to obtain the greatest accuracy possible in the solution of the problem were the objects of the present research.   We were fortunate in being able to profit by previous experience, many of the difficulties having already been surmounted in previous investigations carried out in this laboratory.

Before discussing the present investigation it will be helpful to review briefly the work previously done relating to the oxygen-silver ratio.   Unfortunately no compound of silver and oxygen exists of a nature suitable for exact work.   The two common oxides of silver are far too unstable to yield results possessing any precision and, moreover, the amount of oxygen in even the higher of these oxides is a comparatively small percentage of the whole.   Hence the necessary errors of the determination are greatly magnified in the calculation.   For this reason it is necessary, as Stas realized, to study a compound of silver and oxygen which contains some third element, and various salts are available for the purpose.   Stas himself used chiefly the chlorates, bromates, and iodates for this purpose, determining the ratio $3O : Ag$ by multiplying together the values found by him for the following pairs of ratios, thus:

$$\frac{3O}{KCl} \cdot \frac{KCl}{Ag} = \frac{3O}{Ag}; \quad \frac{3O}{AgCl} \cdot \frac{AgCl}{Ag} = \frac{3O}{Ag}; \quad \frac{3O}{AgBr} \cdot \frac{AgBr}{Ag} = \frac{3O}{Ag}; \quad \frac{3O}{AgI} \cdot \frac{AgI}{Ag} = \frac{3O}{Ag}$$

In each case the first ratio was obtained by the decomposition of a halate (i. e., a chlorate, bromate, or iodate) and the second ratio by the comparison of silver with a halide.   If the exact identity of the halide obtained from each oxygen salt with that employed in the corresponding second process could be proved, and if the various substances had been pure, the method would have been an admirable one; but unfortunately neither of these important qualifications was completely attained.   Moreover, other minor errors crept into the work.[1]

The nitrate and sulphate of silver were also studied by Stas, and his figures concerning these substances may be used in a similar way.   These researches have been recently repeated with greater precision in the chemical laboratory of Harvard College;[2] but here the outcome is complicated by the fact that the relation neither of nitrogen to silver nor of sulphur to silver is precisely known.   Nitrogen, it is true, has been referred with much plausibility to oxygen, with the help of gas densities; but this is a physical rather than a chemical method of determining atomic weights.   Excellent though it undoubtedly is as corroborative evidence, it can not carry with it the conclusiveness which a chemical determination could

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[1] The best discussion of this subject is to be found in Brauner's admirable discussion on the "Fundamental Atomic Weights" in Abegg's "Handbuch der anorganischen Chemie," II, 1, 177-182.

[2] Carnegie Institution of Washington Publication No. 69.

furnish. On the other hand, the atomic weight of sulphur is far from certain.

Without attempting to give a complete historical discussion, the most important results of other investigations may be mentioned. The interesting and valuable results of Dixon and Edgar,[1] of W. A. Noyes and H. C. P. Weber,[2] and of Edgar alone[3] upon the quantitative synthesis of hydrochloric acid furnish less direct evidence upon the matter in hand, for they need the introduction of two other ratios, namely, that of hydrogen to oxygen and that of chlorine to silver, in order to solve the problem. Thus:

$$\frac{2H}{2Cl} \cdot \frac{2Cl}{2Ag} \cdot \frac{O}{2H} = \frac{O}{2Ag}$$

Even if the result were not burdened with all the errors which may reside in the additional figures, it would not be very satisfactory, because oxygen is compared with over thirteen times its weight of silver, and any error becomes greatly magnified in the calculation.

Simpler arithmetical manipulation is demanded by the recent interesting complete analysis by Guye and Fluss[4] of nitrosyl chloride, NOCl, but the result is still somewhat open to the last objection. Thus:

$$\frac{O}{Cl} \cdot \frac{Cl}{Ag} = \frac{O}{Ag}$$

Here the weight of oxygen for a given weight of silver is double that in the last case.

A more promising method has been developed by Baxter,[5] and carried out with the assistance of G. S. Tilley, namely, the direct analysis by decomposition of iodine pentoxide. In this way may be determined with considerable accuracy the ratio $I_2 : 5O$, and by multiplying the results by the ratio of silver to iodine[6] the ratio of $2Ag : 5O$ is at once obtained. Thus:

$$\frac{5O}{2I} \cdot \frac{2I}{2Ag} = \frac{5O}{2Ag}$$

If the second ratio were known with the greatest accuracy, this method would be an excellent one; but the peculiar nature of silver iodide has interfered with the attainment of quite as certain results concerning this substance as concerning the other silver halides.

The values obtained for silver from these various methods range from 107.92, based upon Edgar's value for chlorine and Morley's value for hydrogen, to 107.85, based upon Baxter and Tilley's work with iodine pent-

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[1] Phil. Trans., 205, 169.
[2] Journ. Amer. Chem. Soc., 30, 13 (1908).
[3] Proc. Roy. Soc. London, A. 81, 216 (1908).
[4] Guye and Fluss, J. chim. phys., 6, 732 (1908).
[5] Baxter and Tilley, Journ. Amer. Chem. Soc., 31, 201 (1909).
[6] Baxter, Proc. Am. Acad., 41, 73 (1905).

oxide, and it is safe to conclude that the truth lies between these extremes. Nevertheless, the range of uncertainty (0.07, or distinctly over 0.05 per cent) is far too great for a datum of such importance.

The necessity for further work upon the ratio of silver to oxygen is very evident, and the present paper recounts an extended investigation, protracted over two years, which has furnished entirely new results of a nature apparently more trustworthy than any previously obtained.

As a first step, all substances which might possibly be available for obtaining further knowledge of this very important ratio were scrutinized with the greatest care, in order to determine whether or not a better starting-point might be found. Evidently, from the foregoing remarks, the selection of the substance for this purpose depends upon more than one consideration. In the first place, it is important that the actual weights of the two elements to be compared should not be very different, so that the error in one may not be greatly magnified in a calculation of the other; hence, because the atomic weight of oxygen is much smaller than that of silver, the comparison must involve several atoms of oxygen with one of silver, if possible. For this reason the most highly oxygenated salts were studied first. It is, moreover, necessary to choose a salt of such a nature that the two ratios $\dfrac{MXO_y}{MX}$ and $\dfrac{MX}{Ag}$ may each be accurately determined. With respect to each requirement, the perchlorates seemed to furnish a peculiarly suitable starting-point. It is indeed remarkable that all previous investigators have chosen to work with chlorates in preference to the perchlorates, which are more stable, contain more oxygen, and are more easily obtained pure.

The choice among the perchlorates was determined by the other considerations which must always form an important factor in a choice of this kind, namely, the nature of the substances to be weighed. In order that accurate results may be obtained, it is obvious that all the substances whose precise weights come into consideration should be capable of complete purification and thorough drying, and the great difficulties attending these processes are governed largely by the specific nature of the substances. In order that a substance may be prepared in a pure state, it must be capable of easy crystallization in such a way as to free it from its usually attendant impurities; and in order that it may be dried it must be capable of fusion without decomposition. There are no perbromates, and the periodates are too unstable; among the perchlorates the only substance which corresponds to these specifications seems to be lithium perchlorate, which fuses at 236° and loses no oxygen at 300°. Fortunately, in other respects this substance is peculiarly well suited for the purpose. Its decomposition products, if any, can be accurately determined. It crystallizes well, and its solubility has a large temperature coefficient; therefore

it may be easily prepared pure. It is not deliquescent or markedly hygroscopic in fairly dry air. It can be synthesized from the chloride merely by the evaporation of this salt with a slight excess of perchloric acid, the less volatile perchloric acid easily expelling the more volatile hydrochloric acid. Finally, it contains over 60 per cent of oxygen—probably more available oxygen than any other known compound, not excepting anhydrous hydrogen peroxide. Ten cubic centimeters of the salt, weighing about 24 grams, contain enough oxygen to occupy, under normal conditions, nearly 10 liters, and all this oxygen is lost when the salt is converted into chloride. Lithium has the least atomic weight of any metal, and chlorine the least of any halogen which forms oxygen salts; therefore it is easy to see how this favorable circumstance comes to pass. Such a substance affords a far more satisfactory means of weighing a gas than any attempt to weigh it in an uncombined condition. When one considers the bulky apparatus necessary in weighing gases, with the attendant errors and the unavoidable small weights of gas, it is easy to see the superiority of a process involving a solid salt containing the gas in an exceedingly condensed form. The weighing of hydrogen absorbed by palladium, a method employed in the recent work on the synthesis of water, is an illustration of this point. In the present case we may consider the lithium chloride as absorbing oxygen, but far more efficiently.

Lithium perchlorate was finally chosen, however, only after a careful study of the other perchlorates, in order to make certain that none of the others offered other advantages outweighing those peculiar to itself. Attention was first directed toward silver perchlorate, which is easily prepared by evaporating a solution of the nitrate with excess of perchloric acid and expelling the free acid by heat. The salt is extremely deliquescent and is difficult to dry without slight decomposition. Its fusing-point is so high (486°) that it can not be completely fused before violent decomposition begins, and for the same reason an accurate determination of the water remaining in the salt dried at a lower temperature would be difficult, if not impossible. Silver perchlorate was, therefore, abandoned, although it has one great advantage—it is easily converted into chloride in a current of dry hydrochloric-acid gas even at ordinary temperatures, the process involving no transfer of material. The reaction is not a reduction, anhydrous perchloric acid being formed.

The alkaline perchlorates were next investigated. Potassium perchlorate can not be fused without rapid decomposition. Sodium perchlorate has a lower fusing-point (482°), but it decomposes slowly at this temperature, and hence can not be accurately weighed. All indications therefore pointed to lithium perchlorate, whose virtues have been already described.

The ratio of silver to oxygen can not be determined from this salt, however, until that of lithium chloride to silver is known. Thus, writing the

relation in a manner analogous to that employed in the case of the chlorates:

$$\frac{4O}{LiCl} \cdot \frac{LiCl}{Ag} = \frac{4O}{Ag}$$

Our knowledge of this second ratio (LiCl : Ag) depended upon the doubtful work of Stas, and his was at the best freighted with the known errors entering into this work upon potassium and sodium chlorides. Hence, an essential step in the new work was the determination of this ratio, and incidentally of the true atomic weight of lithium. Even if Stas's value for lithium had been precise, however (instead of as we found it, nearly a whole per cent in error), there would still have been good reason for making this determination anew with the same material used in our work with the perchlorate ratio. If the same sample of lithium chloride is used in determining both ratios, it is evident that the value obtained for the oxygen-silver ratio is independent of any other atomic weight and that the weight of the alkaline chloride is eliminated. It matters not whether this chloride is free from other alkaline metals or contains them. To use an impure lithium salt would be, of course, a waste of time; from such a substance the atomic weight of lithium could not simultaneously be found.

The methods of determining these two ratios $\frac{LiCl}{Ag}$ and $\frac{4O}{LiCl}$ are so widely different that they will be treated separately. While the ratio of silver to a chloride has so frequently been carried out in the Harvard Chemical Laboratory that the operation presents no difficulties, the method for determining the amount of oxygen in the perchlorate was solved only after a long and careful research. The former of the two processes naturally precedes the latter; accordingly the determination of the equivalent of lithium chloride, referred both to silver and to silver chloride, will be found in the first section of this paper. On the other hand, the second section of the paper deals with the preparation of the perchlorate and the determination of the oxygen which it contains.

We take pleasure in expressing our obligation to the Carnegie Institution of Washington for generous pecuniary assistance throughout the course of the work.

HISTORY OF THE REVISIONS OF THE ATOMIC WEIGHT OF LITHIUM.

A glance at table 1, which shows the results so far obtained, reveals wide discrepancies.[1]

TABLE 1.

	Name.	Year.	Ratio.	Atomic weight.	
				Ag = 107.93.	Ag = 107.88.
1	Arfvedson....	1817	LiCl : AgCl	10.1	....
2	Vauquelin....	1818	Li2SO4 : BaSO4..........	9.3	....
3	Gmelin.......	1819	Analysis of Li2CO3.......	9.6	....
			Analysis of Li2SO4.......	10.7	....
			Gmelin assumes	7.65	....
4	Kralovansky..	1827	Li2SO4 : BaSO4..........	10.1	....
5	Hermann.....	1829	Li2CO3 : CO2............	6.1	....
			Li2SO4 : BaSO4..........	6.1	....
6	Berzelius.....	1829	Li2SO4 : BaSO4..........	6.69	....
7	Hagen.......	1839	Li2SO4 : BaSO4..........	6.6	....
8	Mallet.......	1856	LiCl : AgCl	6.96	6.96
			LiCl : Ag	6.92	6.92
9	Troost.......	1857	Li2CO3 preliminary value.	6.5	....
10	Mallet.......	1859	Li2SO4 : BaCl2..........	7.01	....
11	Diehl........	1862	Li2SO4 : BaSO4..........	7.04	....
			Li2CO3 : CO2...........	7.03	7.03
12	Troost	1862	Li2CO3 : CO2............	7.00	7.00
			LiCl : AgCl	6.96	6.96
			Li2CO3 : Li2SO4 (one experiment)	7.13	....
13	Stas.........	1865	LiCl : Ag	7.006	7.003
			Stas himself calculated ...	7.022	....
			LiCl : LiNO3	6.92	6.96
14	Dittmar......	1889	Li2CO3 : CO2...........	6.89	6.89

All excepting one of these determinations was made more than forty years ago, and the most recent, made twenty years ago, involved the use of a questionable method. Hence it is clear that a redetermination of the atomic weight would be desirable, even if it were not essential for the precise evaluation of silver and oxygen with the help of lithium perchlorate. Lithium alone among the five alkali metals has not received reasonable attention in this respect in recent years.

Of these twenty-three values found for the atomic weight of lithium, only those given in the last column of table 1 referred to the standard Ag = 107.88 are worthy of serious consideration. A few words discussing their merits and defects, in chronological sequence, will not be misplaced.

[1]This table is taken from Brauner's admirable chapter on this subject in Abegg's "Handbuch der anorg. Chemie," II, 1, 106. The references to the original papers are as follows: (1) Schweigg. Journ., 22, 93 (1817); (2) Ann. chim. phys., 7, 284 (1818); (3) Gilb. Ann., 72, 399 (1822); (4) Schweigg. Journ., 54, 231 (1827); (5) Pogg. Ann., 15, 480 (1829); (6) *Ibid.*, 17, 379 (1829); (7) *Ibid.*, 48, 361 (1839); (8) Sill, Amer. Journ. Sci. (2), 22, 349 (1856); (9) Ann. chim. phys. (3), 51, 111 (1857); (10) Sill, Amer. Journ. Sci. (2), 28, 349 (1859); (11) Lieb. Ann., 121, 93 (1862); (12) Compt. rend., 54, 366 (1862); (13) Stas, Oeuvres Complètes, I, 710 and 717; (14) Proc. Roy. Soc. Edinburgh, 35, II, 429.

Mallet in 1856 purified his lithium chloride by dissolving it in alcohol and ether; but Stas has shown[1] that by this method the salt can not be separated from the chlorides of the other alkaline metals. He fused and weighed it in a covered platinum crucible—a process which must have given an alkaline product, in spite of the fact that ammonium chloride was added. Moreover, the hygroscopic nature of the chloride prevents it from being exactly weighed without greater protection from laboratory moisture. In two experiments the silver chloride was weighed, and in one the solution was titrated against a known weight of silver, following the method of Pelouze. The latter method in its old form gives too low results. The various errors seem to have counterbalanced one another, for the average value, 6.94, is almost exactly correct. This happy result could hardly have been foreseen, however.

Diehl purified his lithium by repeated precipitation with ammonium carbonate, thirty precipitations being required to free it from sodium. The lithium carbonate was then dissolved in sulphuric acid and treated with barium hydroxide, the lithium hydroxide thus obtained being converted into carbonate. This was dried at 130° and decomposed in a Bunsen apparatus by means of dilute sulphuric acid, the carbon dioxide being determined by the loss in weight of the apparatus. Four experiments were performed, the average value obtained being 7.03, but no vacuum corrections were applied, nor was a counterpoise used in weighing. The possibilities of uncertainty are so great that no one to-day would be disposed to accept the result without question.

Troost purified lithium carbonate by repeatedly dissolving it in cold water saturated with carbon dioxide and reprecipitating it by boiling the solution. In two experiments it was dried at 100°, mixed with powdered ignited quartz, and the carbon dioxide determined by the loss of weight on heating. In one experiment it was converted into the sulphate. In two experiments lithium chloride was dehydrated in dry hydrochloric-acid gas, which was afterwards displaced by dry air. The chlorine was determined by weighing as silver chloride and the mean value obtained for the atomic weight was 6.96. This outcome possesses the virtues and defects of Mallet's work.

Dittmar purified lithium carbonate by the method of Troost, but did not obtain a pure salt. He fused it in a current of dry carbon dioxide, the pressure varying from one to two atmospheres. By this means the formation of oxide was prevented. The carbonate was decomposed by dilute sulphuric acid, the gas evolved being absorbed by potassium hydroxide and weighed. The work was ingenious but very crude, the mean of ten results, varying more than 0.5 per cent, was 6.89.

[1] Stas, Oeuvres Complètes, I, 691.

Stas's work was far more careful than any cited above, although the final result was really not as accurate. He purified his lithium salt according to the methods of Diehl and of Troost. After removing most of the other metals by dissolving the chloride in alcohol and ether, the lithium was precipitated with ammonium carbonate seven times before it was found to be free from sodium. The lithium in the mother-liquors was precipitated as carbonate, and this was purified by conversion into soluble bicarbonate and reprecipitation of the solution by boiling—a very troublesome operation requiring several days. Two such treatments gave a product free from sodium. Both methods are extremely wasteful, 1200 grams of fairly pure carbonate yielding only 145 grams of the purest salt. This was converted into chloride by heating in a platinum boat to 175° in a current of dry hydrochloric-acid gas. The chloride was then maintained in a state of fusion for 20 minutes, and finally cooled in nitrogen, after which it was weighed in a vacuum. The solid salt was subsequently dropped into a solution containing the theoretical amount of silver dissolved in nitric acid, and the titration was carried on exactly as in the work on sodium chloride. The errors incident to this process have been pointed out by Richards and Wells.[1] Impurity in the silver and occlusion of silver nitrate by silver chloride tended to lower the atomic weight; impurity in the lithium chloride and the error of method of determining the end-point tended to raise it. Stas himself calculated as the mean atomic weight of lithium from 3 experiments 7.022; but this becomes 7.003 if modern values for silver and chlorine are substituted.

He also determined the ratio $LiNO_3 : LiCl$ by dissolving the chloride in water in a large flask, evaporating with excess of nitric acid, and finally fusing the nitrate. Using modern values for nitrogen and chlorine, the atomic weight of lithium calculated, from the mean of 3 experiments, is 6.961—a value much more nearly correct than the other.

Stas always found his lithium chloride alkaline to litmus, even when it had been heated in hydrochloric acid until half the salt had volatilized. This fact is not easily accounted for, yet it helps to explain the excessively high value for the atomic weight which he obtained. His lithium chloride volatilized in hydrochloric acid without leaving any residue, but this would not preclude the possibility that chlorides of the other alkali metals were present. In some later work on lithium[2] he failed to obtain, by the means previously employed, a sample of lithium carbonate which would not show the sodium line upon very careful spectroscopic examination. It was necessary to volatilize, in the oxyhydrogen flame, one-third or one-half of the carbonate, in order to obtain a residue of oxide absolutely free from sodium. From this oxide he was unable to prepare pure lithium chloride, and he

[1] Journ. Amer. Chem. Soc., 27, 459 (1905).
[2] Oeuvres Complètes, III, 324.

remarked that he believed it impossible to obtain that salt absolutely free from sodium unless every trace of dust could be excluded. It is obvious that the purification of lithium salts demands further attention.

Up to the present time the most accurate work on this element has been usually supposed to be that of Stas. Since the errors in his work on the chlorides of potassium, sodium, and lithium are similar, and his values for the first two metals are too high, we should naturally expect the same to be true of lithium. The error was quite noticeable in the case of potassium, still more pronounced with sodium, and, as will be shown, was greatest of all with lithium.

In reviewing the foregoing results, which vary so widely, it seemed clear that the reason for the incompatibility of the values obtained for lithium was to be sought not only in the methods of analysis, but also in the impurity of materials. Accordingly the first step of the present research was a careful study of the various practicable methods of purifying salts of lithium. The next procedure was obviously the application to the purest lithium material of the methods already so thoroughly studied in the Harvard Chemical Laboratory in the cases of sodium and potassium. Some of the details of these methods were improved; and these improvements will be described in due course.

BALANCE AND WEIGHING.

The excellent and sensitive Troemner balance which has served in many similar researches was used in the present work. Successive weighings of the same object rarely differed more than 0.02 mg.

The Sartorius gold-plated brass weights and rider were standardized from time to time by the method usually used at Harvard.[1] All weighings were made by substitution, using a counterpoise similar to the object which was being weighed, so that the weights required were never large in amount, and the influence of changes in atmospheric conditions was negligible.

The vacuum corrections applied were as given in table 2, the density of the weights being 8.3.

TABLE 2.

	Density.	Vacuum correction per gram.
Silver	10.49	−0.000030
Silver chloride	5.56	+0.0000732
Lithium chloride [2]	2.068	+0.000436
Lithium perchlorate	2.428	+0.000350

[1] Richards, Journ. Amer. Chem. Soc., 22, 144 (1900).
[2] Baxter, Amer. Chem. Journ., 31, 558 (1904).

THE PREPARATION OF MATERIALS.

All the solid, liquid, and gaseous materials used in this research were purified with the greatest care. The most insidious sources of impurity in work of this kind are dust and the various gases sometimes contained in the air of the laboratory, and the most efficient methods of purification may fail to give a pure product unless careful attention is paid to this fact. The presence of dust, which always contains sodium, was especially noticeable in the preparation of pure lithium salts, where sodium was the element most difficult to remove. It was found that a lithium salt free from sodium, after being recrystallized in the usual way, always acquired traces of this element. The air of the room was therefore kept as pure as possible, and all evaporation and handling of solutions and salts in the final work were conducted in a large glass case. Vessels containing pure material were always kept covered and under bell-jars when not in use. When it was necessary to work under the hood a large, clean glass plate was suspended above the apparatus to protect it from particles of dust falling from above. All heating was conducted electrically in order to avoid the deleterious effects of products of combustion.

Since most of the heating apparatus was constructed in the Harvard Chemical Laboratory during the progress of the work, a brief description of it may not be inappropriate. The resistance material was "nichrome," an alloy of nickel, iron, and chromium, which withstands fairly well a temperature of 1000°. It was generally used in the form of a ribbon, 1.5 to 3 mm. wide. A small electrical stove or hot plate for conducting evaporations was made by winding this ribbon on a quartz plate, which was then covered with another thin plate of the same material, and the whole suitably mounted and insulated with asbestos. Another form, particularly adapted for heating flasks and dishes, was made by winding layers of wet sheet-asbestos and the ribbon concentrically till the desired size was obtained; the roll, while still moist, was then pressed against the vessel to be heated and shaped to fit it. When dry, the mass of asbestos, with its embedded ribbon, retained its form and was mounted on asbestos board. A drying-oven was made by winding a 3-liter beaker with the ribbon and jacketing it with heavy asbestos. By cutting through this jacket at one place a window was formed, through which the interior could be observed. A temperature of 400° was easily obtained. Porcelain tube for fusing silver was wound with the ribbon and covered with thick asbestos. When it was desired to heat a glass tube and at the same time observe the interior the ribbon was left bare, and the convolutions were far enough apart so as not appreciably to obstruct the view. The value of electrical heating, both as to cleanliness and wide range of application, was emphasized in the present research.

The vessels used in purifying materials were usually of quartz or platinum. Where glass was unavoidable, the best Jena glass was employed.

Water.—Distilled water of the laboratory was twice redistilled, once from alkaline permanganate and once alone, using pure tin condensers without rubber or cork connections.[1]   In special cases the water was condensed and collected wholly in platinum.   Dust was carefully excluded by passing the end of the condenser through a hole blown in the bulb of a small flask, which rested on the mouth of the large Jena flask in which the water was collected and stored.   Water was always distilled just before use.

Nitric acid.—Carefully tested pure nitric acid of commerce was redistilled, using a platinum condenser.   When required to be free from chlorine the first portion was rejected and the acid redistilled until it showed no trace of this element when examined in the nephelometer.

Hydrochloric acid.—The pure acid of commerce was boiled with a little pure potassium permanganate, and then repeatedly distilled, using a quartz condenser.

Ammonium fluoride.—Baker's best hydrofluoric acid, which was already very pure, was distilled once in a platinum retort and neutralized by distilling into it, through a platinum tube, pure ammonia from a concentrated solution of the gas.

Ammonium carbonate.—The purest commercial salt was dissolved in water containing ammonia and distilled in a platinum retort.   Any trace of impurities contained in the product must have been volatile ones, which could exercise no harmful effect in the present case.

Hydrazine hydrate.—This substance was prepared by distilling to dryness in platinum a mixture of hydrazine sulphate and potassium hydroxide in solution, using double the theoretical quantity of the latter substance. The resulting solution was distilled again from the small residue of alkali which had been carried over into it; the dilute portion coming over first was distilled yet once more in order to concentrate it, the first fractions, containing almost nothing but water, being rejected.   The substance was collected and preserved wholly in platinum, as were also the ammonia and ammonium fluoride.

Perchloric acid.—This was prepared by a modification of the method of Kreider.[2]   Since sodium perchlorate can now be obtained in large quantities, the preparation of the stable hydrated acid is a comparatively simple operation, quite free from the dangers and difficulties involved in preparing the unstable anhydrous compound.

A saturated solution of sodium perchlorate was poured into 2.5 times its volume of pure concentrated hydrochloric acid (density, 1.20).   After thorough agitation the sodium chloride was allowed to settle, the clear liquid was siphoned off, and the sodium chloride drained in a funnel by

[1] Richards, Proc. Amer. Acad., 30, 380 (1894); Chem. Ztg., 1907, No. 73, 899.
[2] Z. anorg. Chem., 9, 343 (1895); Amer. Journ. Sci. (3), 49, 443; Kreider and Breckenbridge, Z. anorg. Chem., 13, 161 (1896); Amer. Journ. Sci. (4), 2, 263.

suction and washed with a little more acid. The solution, containing hydrochloric and perchloric acids with a little salt of sodium, was evaporated until dense white fumes of perchloric acid began to appear. The liquid was then found to be entirely free from hydrochloric acid. At this point the concentration of the perchloric acid is approximately that of the dihydrate—about 70 per cent. If distilled under ordinary pressure, where it boils at 203°, there is considerable decomposition, involving a loss of perhaps 10 per cent. The crude acid was therefore usually distilled under 150 to 200 mm. pressure, with almost no decomposition; but for the final distillation a pressure of 15 to 20 mm. was not exceeded. At first the acid was condensed in a platinum condenser bent at right angles and having its upper end slightly conical to fit into the constricted neck of a 2-liter flask of resistant glass. The constriction was carefully ground until the platinum fitted it tightly. It was found that this joint held a vacuum very effectively after the flask and condenser had been pressed firmly together. The other end of the condenser passed through a rubber stopper fitted into a hole in a bell-jar containing the platinum dish to receive the distillate. While the excess of water was being distilled off, the acid bumped rather badly; but when the concentration of the acid became that of the constant boiling mixture, this distilled rapidly and smoothly without any sign of ebullition. The yield is practically the theoretical.

Even when distilled under a pressure of 15 mm. the acid had a faint odor, resembling that of the oxides of chlorine. It seemed possible, therefore, that the hot liquid might attack slightly the platinum condenser, although no evidence of such an effect was observed. Accordingly, in preparing the purest acid we decided to condense and collect it in quartz vessels. To the quartz condenser was attached the half-liter distilling flask, into the neck of which was fused a dropping funnel, terminating in a capillary at the bottom of the flask. In this way acid could be introduced continuously during the distillation. The connection between the flask and the quartz condenser gave much trouble. At first a carefully ground joint was used, the quartz forming the inner portion, but it was found that since the co-efficient of expansion of glass is far greater than that of quartz, such a joint will invariably crack, even when exposed to a change of temperature of only 75°. If the outer portion is glass, it cracks on cooling; if quartz, on heating. The only possible joint between these two materials which will allow expansion and contraction is one having two flat faces ground together, as in figure 1. Such a joint is easily made by forming a collar on the end of each tube, grinding them until perfectly plane, and finally polishing with oil and rouge. The two faces are held tightly together by a rubber band or a spring. Such a joint, without any lubricant, held a vacuum very effectively and was entirely unaffected by changes of temperature. The joint was so placed that any condensed liquid coming into contact

with the glass part would run back into the distilling flask.   After at least three previous distillations, the acid was finally distilled through the quartz condenser directly into a quartz flask, and all possibility of introducing impurity in this process was avoided.
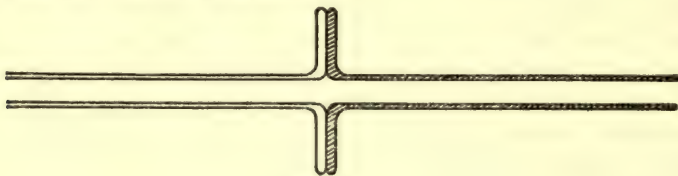

FIG. 1.

The question of the purity of the acid thus obtained was carefully investigated.   All the possible impurities must be those present in the sodium perchlorate and hydrochloric acid, and the only acids likely to remain after concentrating the crude acid are sulphuric and phosphoric; the others are either destroyed or volatilized.

In order to determine how readily sulphuric acid could be separated from perchloric, a mixture of the latter with 2 per cent of sulphuric acid was fractionated.   After three distillations, in which only 10 per cent was rejected, 90 per cent of the last distillate proved to be entirely free from sulphuric acid and 9 per cent more contained so little that the residue left after evaporating off all but 1 c.c. showed a barely visible opalescence upon the addition of barium chloride.   Phosphoric acid is even easier to remove.   The residue remaining after the distillation of the crude acid from 8000 grams of sodium perchlorate, consisting mainly of sodium salts, contained a little sulphate and a trace of phosphate, but the last 20 c.c. of acid distilled from this showed no trace of phosphoric acid.

Since the acid was never distilled less than four times, each time rejecting a small residue, its purity was evidently quite beyond reproach.   If further proof was needed, this was furnished by the fact that the residue of 5 c.c., remaining after distilling off about 8500 grams of acid (previously twice distilled) and which must have contained practically all the sulphuric acid present in the entire amount, showed only the merest trace of it, not over 0.0001 gram.

Silver.—The preparation of pure silver has been fully described by Richards and Wells[1] and the details need not be repeated here.   Four samples were prepared.

Sample A: Pure silver nitrate was recrystallized five times from dilute nitric acid, using vessels of Jena glass.   The crystals were centrifugally drained in platinum funnels.   The silver was then precipitated by ammonium formate, prepared from redistilled ammonia and formic acid, and after thorough washing was fused on pure lime in a current of dry hydrogen,

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[1] Journ. Amer. Chem. Soc., 27, 472 (1905).

generated by the action of "hydrone"[1] on water. The boat was provided with partitions, so that buttons of a suitable size were formed. These were etched with dilute nitric acid, washed, and dried in a vacuum at 400°.

Sample B was prepared in a similar way, except that it was recrystallized twice in glass and four times in platinum, and the reduction with formate was conducted in a platinum dish.

Sample C was obtained by precipitating the mother-liquors from A twice successively with formate, then fusing on pure lime with a blast lamp.

Sample D was prepared from pure silver nitrate which had been once recrystallized, precipitated with formate, and fused on lime in hydrogen. This and sample C were used only as the source of silver nitrate in the precipitation of silver chloride to be weighed.

Experiments were made to determine whether the platinum dish was attacked by the hot nitric acid used to dissolve the silver nitrate, the dish being weighed before and after the operation. There was no loss in weight when the contents of the dish were stirred with a smooth glass rod, but when a platinum spatula was used, and the stirring was very vigorous, a loss of 0.24 mg. was observed, doubtless due to abrasion by its rather sharp edges. The precipitation of silver by formate caused no change in the weight of the dish.

Lithium chloride.—The most common impurities in lithium salts and likewise the most difficult to eliminate are those elements most nearly related to it—the metals of the alkalies and alkaline earths. In the material which formed the source of the lithium chloride used in this work, the only impurities present in appreciable amounts were iron, calcium, potassium, sodium, and probably magnesium. It is true that none of the latter was ever found, but this is probably due more to the difficulty of detecting small traces of it in the presence of large quantities of lithium than to its entire absence. In Kahlbaum's lithium chloride, which formed part of the original material, no calcium, potassium, or magnesium could be found. Since the iron was very easily removed, the impurities whose separation demanded careful investigation were potassium, sodium, calcium, and magnesium. The relative effects of these on the atomic weight of lithium vary in the order given, that of potassium being the greatest.

Attention was first turned to the methods of eliminating potassium and sodium, which go together. Those employed by previous investigators were either inadequate or extremely wasteful. To the first class belongs that of dissolving the chloride or nitrate in a mixture of alcohol and ether. This was found to be effective in removing the greater part of the sodium from a crude chloride, especially if the solution were treated with hydrochloric-acid gas until part of the lithium chloride was precipitated; but aside from this it has no value. Precipitation by means of ammonium carbonate

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[1] This is the trade name for an alloy of sodium and lead.

is effective, but the yield is very small, since only half of the lithium can be precipitated in one operation, owing to the solvent action of the ammonium salts. The conversion of the normal carbonate into bicarbonate demands too great a volume of solution, and is entirely too tedious where large quantities are required.

The most common method of purification—the recrystallization of soluble salts, seems to have received no attention, and accordingly various salts were tested with regard to their fitness for this purpose. With lithium chloride, the amount of sodium steadily decreased upon successive recrystallization until only a trace remained, but this trace was very hard to remove. Moreover, the solubility of the salt is so great that the process is very wasteful. The oxalate was almost useless in this respect. Recrystallization of the formate was fairly effective, but its electrolytic oxidation to carbonate was more so. Both the perchlorate and nitrate gave good yields, and the elimination of sodium was rapid, especially in the case of the nitrate. Care must be taken, however, to crystallize this latter salt below 29.6°, the transition-point between the hydrated salts $LiNO_3.\frac{1}{2}H_2O$ and $LiNO_3.3H_2O$. Above 61° the anhydrous salt crystallizes, and under these conditions the separation from sodium is poor. The perchlorate crystallizes as $LiClO_4.3H_2O$.

These two salts were, therefore, selected as giving the most favorable results, but even with their help it is almost impossible to eliminate the last traces of sodium. It was evident that some method involving precipitation would be necessary. A search among the insoluble salts of lithium showed that the solubility of the fluoride is only 2.7 grams per liter—one-fifth that of the carbonate—and that this solubility is not appreciably affected by the presence of ammonium salts. Sodium fluoride is 16 times and potassium fluoride 340 times more soluble.

Evidently the precipitation of lithium fluoride by ammonium fluoride ought therefore to be an extremely efficient means of removing sodium, without appreciable loss of lithium, and this was found to be true. Solutions of ammonium fluoride and of a lithium salt were run slowly into boiling water in a platinum dish, with constant stirring, taking care to avoid any great excess of either. The lithium fluoride formed under these conditions was coarsely crystalline and the precipitation was practically complete. The precipitate was transferred to platinum funnels and washed several times with water, using centrifugal drainage. Such washing has been shown to be very effective.[1] If the original material contained comparatively little sodium, this precipitate was found to be entirely free from it, upon careful spectroscopic examination; and a repetition of the precipitation was sufficient to attain this end, even with very crude mate-

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[1] Richards, Journ. Amer. Chem. Soc., 27, 104 (1905).

rial. The pure fluoride was then converted into either nitrate or perchlorate by heating in a platinum retort with the corresponding acid—the distillate, when perchloric acid was used, being pure hydrofluoric acid, which was used again. When nitric acid was used, three or four times the theoretical quantity was required, owing to the slight difference in the boiling-points of the acids. Thus it was possible to obtain, rapidly and without appreciable loss, lithium nitrate or perchlorate absolutely free from sodium. Some difficulty was experienced, when making the spectroscopic tests, in obtaining a flame free from sodium, but if the air of the room was not dusty, this could be accomplished by using a small blast flame, supplied with pure washed air.

This method does not, however, eliminate calcium and magnesium, since the fluorides of both these metals are less soluble than that of lithium. Previous treatment of the solution with lithium fluoride is not very effective, but the addition of ammonium oxalate removes nearly all the calcium. The addition of lithium carbonate is yet better, only traces of calcium and magnesium remaining. These may be wholly separated by the recrystallization of the nitrate or the perchlorate. From a sample of lithium nitrate to which had been added 10 per cent each of lithium sulphate and calcium and magnesium as nitrates there was obtained after four recrystallizations a salt which gave no tests for any of these impurities. The recrystallization of the perchlorate was almost equally effective.

The method of purification finally adopted was, therefore, essentially the following: The fluoride, free from sodium but containing possible traces of calcium, magnesium, and sulphate, was converted into nitrate or perchlorate as described. These salts, free from fluorine, were recrystallized several times, using centrifugal drainage. The efficiency of this method may be shown by the fact that 70 grams of free acid were so completely removed from 400 grams of lithium perchlorate by three recrystallizations that less than a milligram of free acid remained. Since even in the mother-liquors from the first recrystallization no calcium, magnesium, or sulphate could be detected by the ordinary tests, there is no doubt that this recrystallized nitrate or perchlorate was exceedingly pure. All silica must have been removed when the fluoride was dissolved in acid. The final step of this sequence of operations alone remained to be taken, namely, the conversion of the salts into chloride.

In the case of the nitrate the conversion into chloride was not difficult. The solution was poured into a hot concentrated solution of ammonium carbonate, which had been distilled in a platinum retort, and the precipitated lithium carbonate was washed several times with hot water, using centrifugal drainage. It is essential that hot and concentrated solutions be used; otherwise the yield of carbonate—which at best is only 50 per cent—will be much smaller. The precipitate is coarsely crystalline and is easily washed.

This process also serves as a means of further purification. The carbonate was dried at 300°, dissolved in slightly less than the theoretical amount of the purest hydrochloric acid which had been twice distilled and condensed and collected in quartz, and subsequently filtered from excess of carbonate. The solution contained a little nitrate, and to convert this into chloride without fear of attacking the platinum a solution of pure hydrazine hydrate, distilled in platinum, was added, and then excess of hydrochloric acid. After boiling the solution a few minutes all the nitrate was reduced, and there remained a solution of pure lithium chloride with a little hydrochloric acid and hydrazine chloride, both of which were completely volatilized in subsequent operations. The chloride was recrystallized once or twice, and dried, and it was then ready for analysis. During purification it was treated only with materials prepared in quartz or platinum.

The conversion of lithium perchlorate into chloride was not so simple. At first the solution was mixed with ammonium chloride and the crystals of ammonium perchlorate were separated by filtration. The solution containing the lithium chloride was evaporated and ignited, but unfortunately on ignition the small amount of perchlorate remaining caused the evolution of considerable chlorine, which attacked the platinum badly. If quartz was used it also was attacked, the salt becoming alkaline. Careful ignition in platinum was the method finally adopted, the presence of the metal being decidedly the lesser evil; but it was necessary to regulate the temperature very carefully, otherwise the action became too violent. The chief action on the platinum occurs only toward the end of the operation, when a higher temperature was required. It was found advantageous to halt the operation at the point where the mass became pasty, to dissolve the product in water, and evaporate to dryness, thus uniformly spreading the perchlorate through the mass of chloride. Sometimes chloride from a previous operation was added. If the final heating was performed in air the platinum was always slightly attacked, but if this were done in an atmosphere of hydrogen the slightly alkaline chloride could be fused without any appreciable effect on the vessel. The chloride thus prepared was freed from platinum and crystallized two or three times and was then ready for analysis. This method of preparation must have given a product absolutely free from traces of other halogens. In all the preparation work exclusion of dust was the greatest difficulty. It was found desirable to shorten all the processes whenever this could be done, so as to expose the material as little as possible. The principal impurity introduced by dust is sodium. It seemed best, therefore, to effect the elimination of the last traces of sodium towards the end of the purification rather than at the beginning.

Several samples of lithium chloride were prepared by these methods, platinum vessels being used throughout. The material which served for the preparation of sample A consisted of chloride prepared from commer-

cial carbonate and freed from most of its sodium by treatment with alcohol and ether. It was recrystallized six times, precipitated as fluoride, and added to another specimen of fluoride which had been precipitated from the mother-liquors, twice recrystallized as perchlorate, and finally precipitated again as fluoride. Subsequently it was all converted into perchlorate, twice recrystallized, treated with ammonium chloride to remove most of the perchlorate, and ignited in platinum. The platinum which was dissolved was removed by a solution of hydrazine, and the chloride was crystallized once more from hydrochloric-acid solution. Owing to an accident in which most of it was lost, this sample was sufficient for only one analysis. It contained a barely visible trace of sodium.

Sample B was prepared from commercial lithium chloride, also purified by solution in alcohol and ether. The main portion was twice precipitated as fluoride. To this precipitate was added some fluoride precipitated from the last mother-liquors of A, and the whole was converted into perchlorate, which was recrystallized three times. It was then treated with ammonium chloride and finally fused in platinum. The platinum which was dissolved was removed, as usual, by precipitation with hydrazine, and the salt was evaporated to dryness. It also contained a trace of sodium.

Sample D: To the mother-liquors from the last three recrystallizations of sample B were added some fairly pure residues of lithium chloride, and the whole was precipitated as fluoride. At this point it was free from sodium. After conversion into perchlorate it was recrystallized six times, ignited to chloride in platinum, fused in hydrogen, and twice recrystallized as chloride. This was D_3. The mother-liquors from these two recrystallizations formed D_4. The mother-liquors from the last three recrystallizations of the perchlorate were once recrystallized; the perchlorate was ignited to chloride and crystallized once. This was D_2. The mother-liquor formed D_1. All these preparations contained a trace of sodium, in spite of the fact that previously the material had been free from this element and no glass vessels had been used. The sodium undoubtedly came from traces of dust.

Sample C: Residues of lithium nitrate and bromide from other work on lithium were treated with ammonium oxalate to remove calcium, and twice precipitated as fluoride. The remainder of sample B was likewise precipitated as fluoride and added to this. All of it was free from sodium. It was converted into nitrate by evaporation in a platinum retort with the purest nitric acid and water, freshly distilled. After expelling all the acid it was dissolved in water and filtered from a slight residue containing fluoride and platinum. The solution contained no platinum and was absolutely free from sodium. The nitrate was recrystallized three times, poured into freshly distilled ammonium carbonate, and the precipitate washed and dried. It was almost completely dissolved in the purest hydrochloric acid,

filtered, more acid added, and then a little hydrazine hydrate. Boiling soon destroyed the nitrate present, and the pure chloride was crystallized once. At last this sample was entirely free from sodium and therefore was worthy to form the basis of some of our best experiments.

Sample E was prepared in much the same way as C. Two kilograms of Kahlbaum's best lithium chloride, nearly anhydrous, were available as raw material. Tested carefully, it showed no potassium, calcium, or magnesium, and only small traces of iron, but as usual it contained considerable sodium. The salt was dissolved in about 8 liters of pure water and agitated with pure lithium carbonate, being allowed to stand over night in large Jena flasks. The precipitate contained iron, but no calcium. The perfectly clear, colorless solution after filtration was evaporated in a platinum dish and crystallized with centrifugal draining, and the mother-liquor was evaporated further, the second group of similarly drained crystals being added to the others. The whole was recrystallized and treated again in the same way. In order to eliminate the small amount of sodium which still remained, the lithium was precipitated as fluoride. The coarse-grained, easily washed precipitate was collected upon a Büchner funnel and was washed two or three times, being each time stirred up with the water. The washed material was whirled in the platinum centrifuge and then washed six times, taking 4 milliliters of water each time and draining completely with centrifugal action after each washing. The last wash-water contained only a faint trace of chloride and the salt was found to be almost wholly free from sodium when examined in the spectroscope. In this way were obtained 620 grams of dry, very pure lithium fluoride, which served as a basis for yet further operations. These successfully removed the traces of impurity still remaining, as the following description shows.

The coarse-grained powder was now decomposed by heating with a large excess of nitric acid in successive additions. About six times the theoretical quantity of 70 per cent nitric acid was required in all, diluted with an equal bulk of water, it having been found that the diluted acid was more efficient than the concentrated acid. After the expulsion of the nitric acid the nitrate was slightly alkaline and no trace of platinum was found by the potassium-iodide test in the filtrate, although the residual precipitate of lithium fluoride contained platinum. In order to be sure that no platinum was present, the clear filtrate was treated with a little hydrazine hydrate, but no change occurred. All the nitrate was finally evaporated with excess of nitric acid until neutralized and the nitrate was crystallized three times with centrifugal drainage in platinum. The trace of sodium present in the fluoride had now entirely been eliminated. The mother-liquors from the last two crystallizations were evaporated and twice recrystallized again, yielding material free from sodium, like the other crystals to which they were added.

The lithium was now precipitated as carbonate—a process which rendered certain the elimination of any traces of fluoride which may have found its way through the successive recrystallizations of the nitrate.

The ammonium carbonate for this purpose was prepared by distilling the substance with water in a platinum still into a platinum dish. The solution was heated to the point of obvious decomposition and the lithium nitrate was then poured into it, the whole being digested for a time at a high temperature. The lithium carbonate was collected in platinum funnels, washed three times with hot water, using centrifugal drainage, and was dried at over 400° in an electric oven. Only about 250 grams of carbonate were thus obtained, a yield of less than 30 per cent of the original fluoride.

The lithium carbonate was then dissolved in hydrochloric acid which had been twice distilled in quartz, rejecting the first and last portion each time. The solution was alkaline, because not quite enough acid had been added to correspond to the carbonate. The filtered solution was treated with a small amount of hydrazine hydrate and a considerable excess of hydrochloric acid. After evaporation, the solution, which had originally given a strong test for nitrate with diphenylamine, was found to be wholly free from this contamination. The purest water was now added, enough to make a hot saturated solution, and the substance was crystallized by cooling the platinum vessel in ice. The crystals were drained centrifugally in platinum and another crop was obtained from the mother-liquor, and the combined material was redissolved and again recrystallized in the same way. In the least pure of the mother-liquors an exceedingly faint trace of sodium was found, but the crystals, after centrifugal drainage, were entirely free from it, as far as the most careful spectroscopic testing could show.

Most of the water was driven off from these crystals over the electric hot plate, and the stirred mass was heated in the electric oven at a high temperature until nearly all the ammonium chloride present had been volatilized. The mass weighed about 170 grams when dry, or about 17 per cent of the lithium originally present as fluoride. A portion of this substance was broken into pieces in a clean warm agate mortar and used in analyses 21–22, 30, and 31.

In spite of the fact that various methods had been used in these purifications and the fact that some of them contained minute traces of common salt, the five preparations were all essentially identical, except from the point of view of the most critical experimenter. The maximum variation affected only the third decimal place in the atomic weight; the second figure was never in doubt. The two purest samples, which were wholly free from sodium, namely, samples C and E, gave exactly the same result, within the limit of error of the experiments. This fact will become manifest when the detailed figures are presented, on pages 31 and 33.

THE DRYING AND WEIGHING OF THE LITHIUM CHLORIDE.

The final preparation of the salt for analysis consisted in expelling the last traces of water by fusion in a platinum boat in a current of dry hydrochloric-acid gas and nitrogen, the operation being conducted in the apparatus usually used for this purpose at Harvard. To avoid absorption of acid by the chloride, this gas was swept out by a current of pure nitrogen, before the salt solidified, and after cooling the nitrogen was replaced by dry air. The boat was then transferred to the weighing-bottle without contact with a trace of moisture, and weighed.

In the preliminary experiments the old form of "bottling apparatus"[1] was used for this purpose, but in the final series, the new form shown in fig. 2 was employed. In this any possibility that moisture might gain
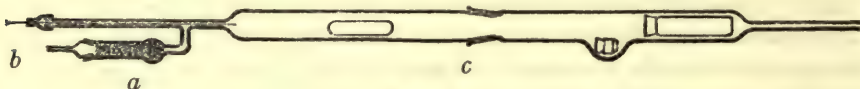
FIG. 2.

access to the salt is excluded; the calcium chloride tube a is not removed and the glass rod used to push the boat into the bottle is passed through a short piece of rubber tubing at b. When this apparatus was constructed of glass evidence was found of the introduction of other alkali-metals into the lithium salt by the action of hydrochloric acid on the red-hot tube. Hence in the final experiments this portion of the apparatus (a to c) was made entirely of transparent quartz and carefully ground into the other. The tube was heated by winding it with "nichrome" ribbon, through which a suitable current was passed, an arrangement that not only gave evenly distributed heat, but also allowed the progress of the fusion to be clearly observed. The apparatus was so constructed that by turning the proper stopcocks either hydrochloric acid, nitrogen, air, or any desired mixture could be passed through it. These stopcocks were so carefully polished with rouge that a trace of lubricant composed of a mixture of paraffin and pure rubber made them perfectly gas-tight.

The nitrogen was prepared by passing air charged with ammonia over red-hot copper. Carbon dioxide was removed by means of potassium hydroxide solution, and the excess of ammonia by passing the gas through a series of towers filled with glass beads moistened with sulphuric acid, the first two containing dilute and the last three concentrated acid. The last traces of water were removed by means of resublimed phosphorus pentoxide. Nitrogen prepared in this way usually contains a trace of hydrogen, which in this case was a distinct advantage, since it would counteract the effect on the platinum boat of any trace of oxygen that might be present.

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[1] Richards and Parker, Proc. Amer. Acad., 32, 59 (1896).

The hydrochloric-acid gas was prepared by dropping concentrated sulphuric acid into a solution of pure concentrated hydrochloric acid. · It was dried by passing through three towers filled with pearls moistened with freshly boiled concentrated sulphuric acid, for it has been shown[1] that phosphorus pentoxide is unsuitable for this purpose. No sulphuric acid could be detected in the solution obtained by passing into water a large quantity of the gas thus prepared.[2]

The air, which was furnished by a water-pump, was purified by passing successively through towers containing potassium hydroxide, silver nitrate, and concentrated sulphuric acid, and was finally dried by phosphorus pentoxide. The entire apparatus was of glass, the different parts being fused together, when possible, or else connected by carefully ground joints.

In detail the procedure was as follows: Dry lithium chloride contained in the platinum boat was placed in the quartz tube and a mixture of nitrogen and hydrochloric acid passed through it for an hour or two, in order to sweep out all the oxygen. The gases issued under slight pressure, the end of the exit-tube dipping just below the surface of mercury, covered with water to absorb the acid. The temperature was very slowly raised so as to expel from the salt as much water as possible before fusion. The chloride was maintained in a state of fusion at a red heat from 15 to 30 minutes, the longer time apparently causing no further change. During this time the surrounding gas consisted principally of dry hydrochloric acid. Bubbles always formed on the bottom of the boat and were removed only by carefully shaking the tube. The hydrochloric acid was then replaced by pure nitrogen, to remove any excess of acid dissolved in the fused salt, and when the issuing gas was neutral the chloride was allowed to cool. It was quite transparent and colorless. Because fused sodium chloride was found to be essentially free from dissolved nitrogen[3] it is reasonable to assume that the similar lithium salt contained no weighable quantity. After the nitrogen had been replaced by dry air the boat was bottled and placed in a desiccator. No great difficulty was experienced in obtaining weighings agreeing within 0.02 mg., using a similar bottle as counterpoise. Of course the bottle containing the empty boat was always filled with dry air before being weighed. The platinum boat was always weighed separately before and after the fusion and the loss in weight, if the operation had been carefully conducted, was only a few hundredths of a milligram— sometimes none at all. This correction, if added to the weight of silver chloride, had no appreciable effect on the results.

The boat was placed in a 3-liter Erlenmeyer flask of Jena glass, with a carefully ground and polished stopper, and about 0.05 or 0.08 liter of water

[1] Baxter and Hines, Journ. Amer. Chem. Soc., 28, 779 (1906).
[2] See also Baxter and Hines, loc. cit., p. 780.
[3] Richards and Wells, Journ. Amer. Chem. Soc., 27, 513 (1905).

was added.   When the chloride was dissolved the solution was perfectly clear, and it was usually tested for alkalinity by adding a very dilute solution of phenolphthalein, which had been colored very faintly pink by a trace of sodium hydroxide.   It is not sufficient to add a colorless solution of the indicator, for the everpresent trace of carbon dioxide decreases the delicacy of the test.   The color never became deeper, and on thorough shaking was discharged by the carbon dioxide.   Methyl orange showed a perfectly neutral tint.   There can be no doubt, therefore, concerning the neutrality of the salt within the narrow limits thus established.   About 1 liter of freshly distilled water was then added to the flask; the boat was lifted out by means of a heavy platinum wire, bent at one end, and was washed seven times in a beaker, the washings being completely transferred to the flask.   This method seemed preferable to dissolving the salt in a beaker and transferring it to the flask, for not more than a few milligrams of lithium chloride could have remained on the boat when it was lifted out, and this small quantity could be transferred without risk of loss.

The lithium chloride was then ready for analysis.   Both of the familiar methods for finding the amount of chlorine were used, namely, the weighing of the precipitated silver chloride on the one hand and the determination of the necessary amount of silver on the other.   These are discussed below in order.

THE PRECIPITATION AND WEIGHING OF SILVER CHLORIDE.

The precipitation of the silver chloride and all subsequent operations were carried out under red light in the dark-room.   To the solution of lithium chloride was added exactly the calculated amount of silver dissolved in a moderate excess of nitric acid, the concentrations of the solutions being about decinormal.   The mixture was shaken vigorously for 10 minutes and allowed to stand over night.   The next day it was again shaken, and to it was added the excess of silver nitrate required for complete precipitation—about 0.05 or 0.06 gram of silver per liter.   This method diminishes greatly the danger of occlusion of silver nitrate, as Richards and Staehler have shown.[1]   The solution was shaken from time to time during the next day, and after standing until the supernatant liquid was perfectly clear it was ready for filtration.

In a few of the preliminary experiments the Gooch perforated platinum crucible with asbestos mat was used, with all the precautions previously adopted in the Chemical Laboratory of Harvard College.   In all others a Gooch-Munroe crucible[2] was used.   The complete removal of silver chloride from the platinum sponge, when preparing for a new analysis, required treatment with concentrated ammonia for at least 12 hours, followed by a

[1] Journ. Amer. Chem. Soc., 29, 632 (1907); Richards and Staehler, Carnegie Institution of Washington Publication 69, page 15 (1909).
[2] Snelling, Journ. Amer. Chem. Soc., 31, 456 (1909).

very thorough washing.   The crucible was always dried over night at 250°, and a perforated platinum plate was placed upon the sponge to prevent rupture by the contraction of the silver chloride as it dried.   This crucible was of the special shape recently described by one of us.[1]

The clear solution was poured through the crucible, and the precipitate was washed four times by decantation with a cold acid solution of silver nitrate, about two-hundredth normal, the precipitate being thoroughly agitated by rotary shaking each time.   The filtrate and washings were united and were always practically free from excess of chlorine, so that a constant correction of 0.04 mg. of silver chloride per liter was applied to them.[2]   The precipitate was then washed ten times with very dilute nitric acid, cooled in ice to reduce the solubility of silver chloride, and finally transferred to the crucible by means of a jet of pure, cold water from a hydrostatic wash-bottle.   The entire process was conducted under a clean pane of glass to prevent dust from falling into the crucible.   The latter was finally wiped with a clean cloth and heated in an electric oven, gradually increasing the temperature to 250°, where it was maintained at least 10 hours.   After it had been weighed the main mass of silver chloride was separated from the platinum disk and fused in a covered quartz crucible contained in a larger one of porcelain.   Since the cover was transparent it was possible to free the fused chloride from the bubbles which invariably adhered to the crucible, without danger of loss from spattering, by carefully rotating the crucible.   With one or two exceptions the fused silver chloride was perfectly colorless and transparent, showing the absence of organic dust and occluded silver nitrate.   The loss on fusion was very small, never more than a few hundredths of a milligram per gram.   The correction for the entire weight of silver chloride was calculated as usual from that of the portion fused, always over 90 per cent of the total.

The flask was carefully rinsed out with ammonia, to remove any chloride that might have escaped observation.   This, with the washings, was tested as follows: To the total washings, exclusive of those with dilute silver nitrate, was added 0.07 gram of silver as nitrate, and after the opalescence had appeared it was dissolved by pouring in the ammoniacal rinsings. The volume was then made up to 1 liter.   A standard solution was prepared, containing in 1 liter a known amount of chloride, and the same quantity of ammonia and of silver present in the washings; 25 c.c. of each solution was pipetted into a nephelometer[3] tube, 2 c.c. of dilute nitric acid added to each, and the contents stirred with a carefully cleaned glass stirrer.   The tubes were covered with glass caps having a plane top, and allowed to stand from 3 to 5 hours, until constancy was attained.   If the

[1] Richards, Journ. Amer. Chem. Soc., 31, 1146.

[2] Richards and Wells, ibid., 27, 487, 517 (1905).   See also] Baxter, ibid., 28, 1322 1906).

[3] Richards and Wells, Amer. Chem. Journ., 31, 235 (1904).

tubes were not nearly alike a new standard was prepared. Several comparisons were always made and found to agree within reasonable limits of error only when extreme care was used in preparing the solutions and in excluding dust. By the use of ice-cold wash-water the total nephelometer correction was reduced from over 1 mg. to about 0.35 mg., often less, owing to the decrease in solubility of silver chloride. This matter will subsequently be discussed in detail. Table 3 gives the results of the preliminary experiments.

The first two analyses have little value, since the technique of the process had not then been mastered and the material was purified only by 6 recrystallizations as chloride, and was known to contain impurities. No. 10 was rejected because it was found that all the silver chloride from the previous analysis had not been dissolved out of the Munroe crucible.

TABLE 3.—*Ratio of Lithium Chloride to Silver Chloride—Preliminary Series.*

No. of analysis.	Preparation of LiCl.	Weight of fused LiCl, vacuum.	Weight of fused AgCl, vacuum.	$\frac{LiCl}{AgCl}$	Atomic weight of Li. Ag=107.88
1	0	4.01994	13.59125	0.295774	6.938
2	0	6.32840	21.39635	.295770	6.939
3	A	8.99620	30.41341	.295797	6.942
4	B	4.66824	15.78111	.295812	6.944
5	B	5.43032	18.35734	.295812	6.944
6	B	5.10725	17.26504	.295815	6.944
8	D_1	5.74000	19.40375	.295819	6.945
9	D_2	5.42038	18.32417	.295805	6.943
11	D_3	5.21573	17.63280	.295797	6.942
12	D_4	6.56925	22.20716	.295817	6.945
13	D_3	4.84268	16.37121	.295805	6.943
					6.943

In none of these analyses was the material wholly above reproach, for it all contained traces of sodium. Part of this impurity was present in the original salt, and those specimens (A and D_3) which show less sodium in the spectroscope gave a lower value for the atomic weight. Part of the sodium, however, may perhaps have come from the glass tube used to contain the boat in which the lithium chloride was fused. This conclusion was drawn from the fact that material thus fused showed in the spectroscope more sodium than it had possessed before. Nevertheless, these preliminary results are far nearer the truth than the work of any other experimenter.

In order to avoid the vitiating circumstances every conceivable precaution was taken in the final series. Both the samples of lithium chloride used were proved to be free from any visible trace of sodium discernible upon careful spectroscopic examination. This means, of course, a very high degree of purity. Moreover, the platinum boat during the fusion of the salt was contained in a tube of pure quartz. In this way only can a pure

dry sample of lithium chloride be obtained, which will show no trace of sodium in the spectroscope.

As a result of these precautions the values of the atomic weight obtained were appreciably lower than those of the preliminary series, and they agreed distinctly better among themselves.

Table 4 explains itself. Analyses 19 and 20 were omitted because of accidents which rendered them valueless. Experiments 14 to 17 inclusive had previously been used for determining the weight of silver needed for the exact precipitation. This part of these experiments is recorded in table 6, under the numbers 26 to 29.

TABLE 4.—*Ratio of Lithium Chloride to Silver Chloride—Final Series.*

No. of analysis.	Prepara-tion of LiCl.	Weight of fused LiCl, vacuum.	Weight of fused AgCl, vacuum.	$\dfrac{LiCl}{AgCl}$	Atomic weight of Li. Ag=107.880
14	C	6.28662	21.25442	0.295779	6.9391
15	C	5.82076	19.67873	.295790	6.9407
16	C	6.70863	22.68030	.295791	6.9409
17	C	6.24717	21.12073	.295784	6.9399
18	C	5.50051	18.59600	.295790	6.9407
21	E	8.34521	28.21438	.295779	6.9391
22	E	6.65987	22.51564	.295789	6.9406
		45.56877	154.06020	.295786[1]	6.9401

[1]Average.

Comparison of these results is highly interesting and leaves no doubt concerning the atomic weight of lithium. The average result for the atomic weight of lithium, computed from these final results taken together, is 6.9401, with a "probable error" of 0.0002.

It is pleasing to note that the average (6.9403) of experiments 14 to 18 inclusive, made with sample C of lithium chloride, is almost identical with the average (6.9399) of experiments 21 to 22 made with sample E. The difference between the averages is only 0.0004, and the average of the first five lies between the values given by the last two experiments. The extreme range is only from 6.939 to 6.941, whereas the extreme range in the preliminary series was from 6.938 to 6.945.

The agreement of these two samples made from different raw materials and purified in somewhat different ways seems to leave no doubt concerning the validity of the result except in so far as constant errors in the methods of analysis or constant unavoidable impurities are concerned. The former of these causes of uncertainty is rendered highly improbable by the next series of experiments, to which attention is now directed.

THE RATIO OF LITHIUM CHLORIDE TO SILVER.

A single series of experiments is never convincing in work of this kind; accordingly the preceding determinations were supplemented by others, which determined the exact amount of silver necessary to precipitate the chlorine in weighed amounts of lithium chloride. No important difference in the final value was expected, because sodium and potassium showed none under similar conditions; but the further work had the advantage of making "assurance double sure."

In this series of experiments weights of the purest silver, equivalent to those of the lithium chloride, as calculated from the preceding table, were dissolved in nitric acid in a Jena flask provided with a tower of bulbs to prevent loss by spattering. Almost the exact amount of silver could be weighed out directly, by selecting suitable pieces from a large assortment of very fine globules; and the last few hundredths of a milligram were added, if necessary, in the form of a standard solution, prepared from the same silver. The solution of silver nitrate was diluted to about 1 liter and added to the solution of lithium chloride exactly as in the preceding series. Great care was used to transfer every trace of silver from the flask. After standing for a day or two, with occasional violent shaking, the presence of an excess of silver or of chlorine was then determined with the nephelometer, following the procedure adopted by Richards and Wells.[1]

One very important innovation was introduced. The accuracy with which the end-point can be determined by this method is almost inversely proportional to the concentration of the silver halide remaining in solution, because the percentage accuracy of the nephelometer does not increase with increasing cloudiness. It has long been recognized that the titration of bromides is more exact than that of chlorides, because the solubility of silver bromide is less than one-tenth of that of the chloride. These considerations show that any means of decreasing the solubility of silver chloride will increase the precision of the end-point. The solubility of silver chloride in water changes greatly with the temperature,[2] being over four times as great at $34°$ as it is at $1.5°$. It seemed worth while, therefore, to try the effect of cooling the solution in ice. Analysis 3 was made to test this point. At this time the weather was quite warm, the temperature sometimes rising above $30°$. The solubility was tested on fourteen successive days, the flask being shaken each day. It was found to vary from 2.2 mg. to 3.4 mg. per liter; the presence of nitric acid was undoubtedly responsible for a higher average value than Kohlrausch's. Opalescences produced by the precipitation of the chloride in such a solution are so intense that it is difficult to estimate accurately their contents in the nephelometer. The flask was then packed in ice, and the solubility again determined for several

[1] Journ. Amer. Chem. Soc., 27, 502 (1905).
[2] Kohlrausch, Z. physik. Chem., 64, 148 (1908).

days. It became very constant, varying from 0.5 to 0.6 mg. per liter. Most of the values obtained were about 0.5 mg., a figure which begins to be comparable with that for silver bromide at ordinary temperatures—0.12 mg. The opalescences were so faint that the slightest excess of silver or of chlorine was unmistakably evident. Richards and Wells estimated that they could detect a difference of 0.02 mg. of silver per liter; this limit we have doubtless reduced by cooling. Assuming the weight of lithium chloride to have been accurate to within 0.02 mg., there could not have been an error exceeding 0.05 mg. in the weight of silver, since the total volume was only 2.5 liters. The determination by this new method of the weight of silver required is evidently the most accurate part of the analysis, and the cause of the variation in results must be sought elsewhere. There is, moreover, another advantage in this method. Since the concentration of silver chloride in solution is constant, at the constant low temperature, it is possible to calculate with greater exactness than before the amount of a deficiency of either silver or chloride, in terms of the ratio of lengths of the two nephelometer columns giving equal apparent opalescences. This advantage hastens the work.

Only two preliminary experiments were made, for the technique required by the determination is so simple that it is readily mastered. The results of these two preliminary experiments, with material not perfectly free from sodium, are given in table 5, and agree almost exactly with the preliminary experiments made by the other method with similar material, as may be seen by referring to table 3. As stated, these preliminary experiments are, of course, entirely neglected in this comparison of final results.

TABLE 5.—*Ratio of Lithium Chloride to Silver—Preliminary Series.*

No. of experiment.	Continuation of analysis.	Preparation of LiCl.	Weight fused LiCl, vacuum.	Weight of Ag, vacuum.	$\frac{LiCl}{Ag}$.	Atomic weight of Li. Ag=107.88
23	3	A	8.99620	22.89013	0.393017	6.942
24	7	B	5.25395	13.36777	.393030	6.943
					.393023[1]	6.942

[1] Average.

All of the preparations used in this preliminary work contained traces of sodium, which would, of course, raise the apparent atomic weight of lithium, and accordingly these early values, if included in the calculation, would introduce a source of error. The experiments were, nevertheless, of great value to the investigators in the course of the work; therefore they seemed worthy of brief notice.

After the various processes had been mastered, the final series, using the utmost care to exclude all sources of error, was undertaken. The experiments were consecutive. The method is simple, and accident is easily avoided. Four of the experiments (Nos. 26 to 29 inclusive) were utilized

further by weighing the precipitated silver chloride.   This portion of the experiment received in each case another number, and the results are given as experiments 14 to 17, inclusive, in table 4.

TABLE 6.—*Ratio of Lithium Chloride to Silver—Final Experiments.*

No. of analysis.	Continuation of analysis No.	Preparation of LiCl.	Weight fused LiCl, vacuum.	Weight of Ag, vacuum.	$\frac{LiCl}{Ag}$.	Atomic weight of Li. Ag=107.88
25	..	..	5.82422	14.82035	0.392988	6.9386
26	14	C	6.28662	15.99687	.392991	6.9389
27	15	C	5.82076	14.81122	.392997	6.9396
28	16	C	6.70863	17.07038	.392998	6.9397
29	17	C	6.24717	15.89620	.392998	6.9397
30	..	C	7.75349	19.72977	.392984	6.9382
31	..	E	7.99108	20.33415	.392988	6.9386
			46.63197	118.65894	.392992	6.9390

These experiments, then, point to the number 6.9390 as the atomic weight of lithium, a number possessing a so-called "probable error" of less than 0.0002.   It will be observed that the maximum deviation from the mean of all the experiments was less than 0.001 in the atomic weight of lithium, a quantity which corresponds to only about 1 part in 65,000 of the lithium chloride.   This is about as high a grade of accuracy as has usually been attained in atomic-weight work.   It means about 0.1 mg. in weight of the substance taken, though the error is probably not to be traced to the work, but rather to inevitable complications in the chemical part of the various processes, especially to occlusion of soluble salts by the silver chloride.

DISCUSSION OF THE FINAL RESULTS.

Thus two final results have been obtained for the atomic weight of lithium, namely, 6.940 by reference to silver chloride and 6.939 by reference to pure silver.   The close agreement of these values is important evidence of their verity, and there seems to be no doubt that the value 6.94 may be taken with great certainty as representing the true atomic weight of this lightest of the metals, supposing that silver is called 107.88.   A change of 0.01 in the atomic weight of silver causes a corresponding change of only 0.0006 in that of lithium.

The reasons for the higher atomic weight found by other experimenters are not far to seek.   Stas admitted that his lithium chloride was alkaline, a circumstance which would, of course, have raised the apparent atomic weight, and it is probable that further error was introduced by other impurities.   Judging from the difficulties encountered in the present work, his methods of purification must have been entirely inadequate.   In those cases in the work of others where the approximately correct value of lithium had been found, the fortunate result must be attributed rather to a compensation of errors than to any special excellence.

The fact that the two series of results gave essentially the same atomic weight of lithium shows that they indicate very nearly the same atomic weight of chlorine, referred to silver, as that found in the work of Richards and Wells. The average of the present work shows that one part of pure silver would give $\dfrac{0.392992}{0.295786} = 1.32864$ parts of chloride, while Richards and Wells obtained 1.32867. This shows that the silver must have been pure within 1 part in 40,000, a fraction about equal to the experimental error of the analysis. One pair of experiments, namely, the pair numbered 16 and 28, gave exactly the value found by Richards and Wells.

Another method of comparing these results is to reduce them both to the ratio of lithium chloride to silver. On this basis, if 1 part of silver chloride corresponds to 0.295786 part of lithium chloride and 1 part of silver corresponds to 1.32867 parts of silver chloride,[1] then 1 part of silver must correspond to 0.393002 part of lithium chloride. This obviously differs by 1 part in 40,000 from the result 0.392992 found directly. The mean of these two figures, namely, 0.392997, may perhaps be supposed to represent the true value of the ratio to within 1 part in 80,000. This value will be chosen for the computation involved in the subsequent work.

SUMMARY.

In conclusion of the first part of the work, the following brief summary presents the chief features. Lithium salts were in the first place studied with great care in order to discover the most suitable substance for the investigation and the best methods for purifying them. The precipitation of lithium as fluoride and the conversion of this precipitate into nitrate or perchlorate with many recrystallizations of the soluble salts was found to be the surest method of eliminating impurities, especially sodium. The perchlorate was decomposed by heat; the nitrate precipitated by ammonium carbonate in order to convert it into chloride. The purer the material the lower was the observed atomic weight of lithium, and the two purest samples gave precisely the same results within the limit of error of experimentation. In all, 45.56877 grams of lithium chloride yielded 154.0602 grams of silver chloride, corresponding to 6.940 as the atomic weight of lithium. Moreover, 46.63197 grams of lithium chloride were found exactly to precipitate 118.65894 grams of silver, corresponding to the value for the atomic weight 6.939. These essentially identical results may be taken to represent the atomic weight of lithium, if silver is taken with the International Committee to be 107.88. If each of these results is given equal weight and 100,000 parts of silver are assumed to produce 132.867 parts of silver chloride, the corresponding amount of lithium chloride is 39.2997 parts.

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[1] Richards and Wells, Carnegie Institution of Washington Publication No. 28, 65 (1905).

PART II.

THE RATIO OF OXYGEN TO LITHIUM CHLORIDE.

PRELIMINARY EXPERIMENTS.

The reasons which led to the selection of lithium perchlorate as the salt to be used in determining the ratio between oxygen and silver, and the advantages of this substance, have already been mentioned briefly in the introduction. Part I of this paper[1] has described the determination of the atomic weight of lithium—an essential link in the chain of data.

After lithium perchlorate had been found to be susceptible of fusion without decomposition—thus being rendered anhydrous and suitable for accurate weighing—a method had to be devised for obtaining experimentally the ratio of perchlorate to chloride, and hence the ratio of oxygen to the chloride and to metallic silver.

Naturally, the first attempts were directed toward the quantitative conversion of perchlorate into chloride. Simple ignition first suggested itself, but was quickly abandoned, because this process involves a loss of chloride, unless extraordinary precautions are taken. The oxygen evolved carries with it particles of the salt so extremely minute that they color a flame 15 or 20 feet distant if the operation is performed in an open dish. To retain this dust would require such an elaborate apparatus that accurate weighing would be out of the question.

A means of reducing the perchlorate was then sought which would prevent this evolution of oxygen, but this proved futile; for, as Kreider has shown,[2] perchloric acid is, in combination, one of the most stable of the oxygen acids, and is hardly affected even by the strongest reducing agents. Hydrogen is entirely without action on the fused salt at 300°, and hydrochloric acid was found to displace only very little of the perchloric. In aqueous solution the situation is not much more promising. Although chlorates in solution are readily reduced, perchlorates under the same conditions are almost entirely unaffected by the most powerful reducing agents, with the exception of ferrous hydroxide and titanous salts, which, in large excess and upon long boiling, reduce them to chlorides.[3] This method is, however, quite unsuitable for precise work. All attempts to convert per-

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[1] See the preceding pages.
[2] Amer. Journ. Sci., 50, 287 (1895); Z. anorg. Chem., 10, 277.
[3] Sjollema, Z. anorg. Chem., 42, 127 (1904); Rothmund, *ibid.*, 62, 108 (1909).

chlorate into chloride, therefore, had to be abandoned, and the reverse process was considered.

The vapor from a constant-boiling mixture of perchloric acid and water, both alone and mixed with additional steam, was passed over lithium chloride at different temperatures; but although some hydrochloric acid was expelled, the conversion into perchlorate was only partial. Frothing and creeping occurred, with unavoidable loss of material. The anhydrous acid was not tried, for its use is highly inconvenient or even dangerous; and after an examination of the thermochemical relations involved there was no reason for supposing that it would be any more effective than its hydrate, which has a higher boiling-point. Recourse was had, therefore, to a method similar to that used by Richards and Forbes[1] in the synthesis of silver nitrate. Lithium chloride was dissolved in water in a quartz flask, a slight excess of perchloric acid was added, over and above the amount needed to convert the salt wholly into perchlorate, and the solution was evaporated by allowing a current of air to pass through the flask, the temperature being regulated so that no ebullition occurred. The hydrochloric acid was soon expelled, and by gradually raising the temperature the excess of perchloric acid was volatilized, leaving pure, fused lithium perchlorate. The substances in the flask were thus changed gradually from a solution of the chloride into pure fused perchlorate, without the formation of a single bubble of gas or vapor. Hence the process is capable of the greatest accuracy.

Further experiments, planned in order to test details of the operation, showed that pure, neutral perchlorate, prepared by recrystallization, could be heated to 300° without decomposition. On the other hand, the salt formed in the above process always contained a trace of chloride and chlorate—as shown by its giving off oxides of chlorine when moistened with perchloric acid. This small amount, however, did not increase on further heating—a fact which indicated that it must have been formed during the evaporation of the excess of acid. This train of circumstances suggested that the impurities might be due to a decomposition of the last traces of acid, which are evolved only at a high temperature and in a nearly anhydrous condition. Since the anhydrous acid decomposes readily, while the dihydrate is very stable, it seemed reasonable to suppose that if the last traces of acid were removed at the lowest possible temperature and in a current of air saturated with moisture (to prevent the dissociation of the dihydrate) this decomposition ought to be prevented, and a salt almost, if not quite, free from chloride obtained. This was found to be true. The purity of the perchlorate obtained depends upon the care with which the excess of acid is expelled before the temperature attains a high point.

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[1] Journ. Amer. Chem. Soc., 29, 808 (1907).

THE CONVERSION OF LITHIUM CHLORIDE INTO PERCHLORATE.

The determination of the ratio of lithium chloride to oxygen thus resolved itself into the following processes: Lithium chloride was to be fused and weighed in a boat just as described in Part I; it was then to be dissolved in a slight excess of perchloric acid; the hydrochloric and perchloric acids were to be driven out by steam; and the fused perchlorate was to be dried at 300° and finally weighed. The gain in weight of the salt is caused by oxygen alone and gives at once the ratio $O_4 : LiCl$. From the known ratio of lithium chloride to silver, the atomic weight of the last-named element is to be calculated.

The general method having been indicated, the complete details of the operation and the apparatus used will now be described. The preparation of very pure perchloric acid and lithium chloride has been already discussed in Part I.

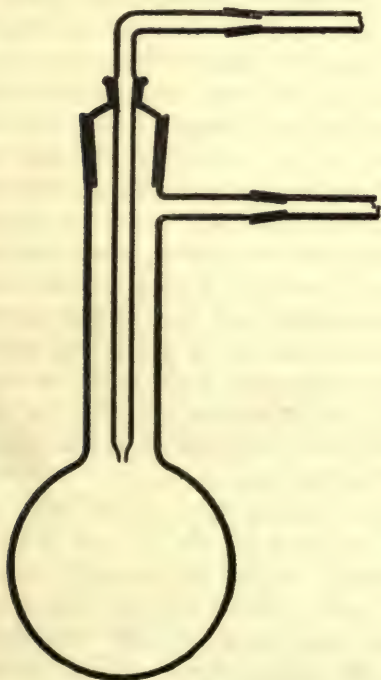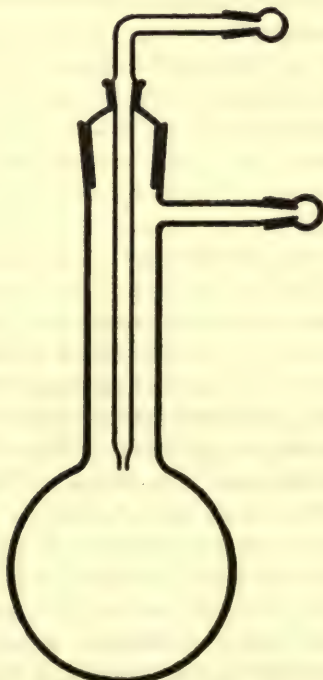FIG. 3.   FIG. 4.

The quartz flasks, of 100 c.c. capacity, which served to conduct the quantitative evaporation, were made especially for the work by Heraeus. They are shown in cross-section in figs. 3 and 4, and may be called evaporating flasks.

The quartz stopper was provided with a ground joint, into which fitted the bent quartz delivery-tube. This tube could be removed and replaced

by a small quartz stopper if desired. The ends of the delivery and exit tubes were ground to fit glass tubes (as in fig. 3), which were attached during the evaporation, and after the operation was finished were replaced by glass caps, which effectually closed the flask (fig. 4). A loop of platinum wire fastened around the neck of the flask served to suspend it from the balance while it was being weighed. One of the flasks was used as a counterpoise. They were kept in separate large Hempel desiccators, with sticks of potassium hydroxide, and supported on baskets of platinum wire. Before weighing the empty flask it was always heated to 300° and dry air was passed through it for a short time, in order to remove any adsorbed moisture, and the flask then allowed to cool in a desiccator. As a matter of fact, experiment showed the same weight was obtained if the flask was filled with dry air at the ordinary temperature, but as a precaution it was always heated.

Platinum seemed to accelerate the decomposition of perchlorate by heat, as might have been expected; and the presence of this metal was, therefore, to be avoided. Hence it seemed desirable to fuse the lithium chloride, the accurately weighed factor in the reaction, in a quartz boat, which could then be left in the evaporating flask during the subsequent conversion to perchlorate. The troublesome transfer of its contents would thus be avoided. Careful quantitative experiments showed that lithium chloride could be fused in quartz in a current of hydrochloric acid without attacking the boat in the least; but unless the walls were very strong it was cracked by the contraction of the fused salt as it cooled. A heavy-walled boat meant a smaller capacity for the fused chloride, and since it was desired to employ the maximum possible amount, the use of quartz was abandoned. A boat of platinum-iridium was especially made to fit into the flask, and used thereafter for the fusion of the lithium chloride. At one end was a slight projection provided with a hole, through which was passed the platinum wire that served to lower the boat into the flask.

The fusion and weighing of the lithium chloride have already been described in the first part of this paper, and need only be referred to here. The boat containing the fused and carefully weighed chloride was lowered gently into the neck of the evaporating flask, to which had just been added a few cubic centimeters of purest water direct from the still. The flask, with the boat suspended in the neck, was placed over an electric heater, covered by a large bell-jar and kept warm over night. The aqueous vapor condensing on the chloride dissolved it, and the solution flowed down into the bulb of the flask. If time were an object, the boat was lowered directly into the water and the contents dissolved in a few minutes; but this method required more water than the other. In either case the final washing was accomplished as follows: To a wash-bottle was attached a glass tube terminating in a capillary, bent sharply at the end at right angles and cut off

so close that it was very little thicker than the rest of the capillary and could be passed between the boat and the walls of the flask.   By means of this fine horizontal jet of water the boat could be washed on all sides and within.   Since the wash-bottle was of Jena glass, and the water was allowed to remain in it only a few minutes, no appreciable amount of alkali could have been introduced in this way.

The boat was then lifted out and carefully rinsed in a beaker, the washings being tested in the nephelometer for chloride.   The amount found was never more than a few hundredths of a milligram.   This correction, when appreciable, was applied to the weight of lithium chloride.

A slight excess of the purest perchloric acid, which had been condensed and collected entirely in quartz, was now added.   The contents of the evaporating flask were thoroughly mixed, and the flask was placed on a support of platinum wire in an electric oven.   The oven was made especially for this purpose by winding a 3-liter beaker with resistance ribbon, a window being provided through which the flask within could be observed.   The stopper and delivery-tube were inserted into the flask, and the delivery-tube was connected by a ground joint with the source of moist air.   The exit tube, passing through a hole in the side of the oven, was connected with a water-pump to remove the acid vapors.   The oven was provided with a glass cover, suitably perforated to admit the thermometer and the delivery-tube.

The air, supplied by a water-pump, was purified by passing successively through towers, some containing potassium hydroxide solution with a little manganate, and others containing a 50 per cent solution of phosphoric acid, to which had been added potassium permanganate.   Thus the air was freed from soluble impurities.

When dry air was desired, the current was passed through further tubes containing, respectively, fused potassium hydroxide and resublimed phosphorus pentoxide.   When moist air was desired it was passed through an electrically heated gas washing-bottle containing water.   By turning the proper stopcocks either moist or dry air could be passed into the evaporating flask.   To prevent the condensation of water in the tube, the latter was wound with resistance wire from the bottle as far as the point connecting it with the quartz flask, and heated by the passage of a suitable current.   The temperature of the oven containing the evaporating perchlorate solution was read on a thermometer, the bulb of which was placed in contact with the evaporating flask as close to the fused salt as possible.

The temperature of the oven was kept at 130° while dry air passed through the flask until about two-thirds of the water had evaporated; then it was raised to 150° until most of the hydrochloric acid had been expelled. Moist air was at this stage passed through the evaporating flask, and soon perchloric acid was evolved.   After several hours at 160° no more appeared;

at 180° a little more was expelled, and from this point the temperature was slowly raised to 250°. The salt was then neutral but not quite anhydrous. To remove the last traces of water, it was heated in dry air at 280° to 300° for at least 5 hours; further heating was found to cause no diminution in weight. The entire operation usually occupied 3 days. The perchlorate was allowed to cool in the current of dry air until the crystals began to appear. It was then warmed to the fusing point (236°) and allowed to cool very slowly, so as to avoid too violent solidification. It was quite crystalline and transparent. The glass caps were then placed over the ends of the tubes and the flask was quickly removed to the desiccator, which was placed for a sufficient time beside the balance-case in a room kept at nearly constant temperature.

The possibility that solid material which ought to be weighed might be carried away with escaping gas and vapor during the evaporation was duly considered. Experiments already made with silver nitrate[1] make it unlikely that this was the case. The method of evaporation seems to be really quantitative. Nevertheless, although no mechanical loss is apparent, there is a conceivable possibility that traces of the lithium perchlorate might be carried away in the state of vapor with the escaping perchloric acid or water at the high temperature. Unlikely as this might seem, it is nevertheless worth testing, and the test was easily applied by adding perchloric acid and water after the fused substance had been weighed and then repeating the evaporation, fusion, and weighing. The interpretation is somewhat complicated by the fact that the true weight of perchlorate can never be attained with perfect accuracy until one knows how large an amount of chloride and chlorate have been formed during the fusion. Rarely were these impurities wholly absent. Nevertheless, the following test is fairly satisfactory.

A neutral solution of nearly 14 grams of pure lithium perchlorate, after various preliminary trials in order to find the best succession of temperatures for the evaporation, was treated with a few drops of an excess of perchloric acid, and the acid was evaporated at 165° for several hours until the mass solidified. The temperature was now raised to 200° and kept there until the mass which had partially melted had again solidified; again gradually raised to 245°, and kept there for less than 2 hours; yet once more gradually raised to 280°, where it was kept for 5 hours, and finally to 300° for yet 3 hours more. After making the correction to vacuum, the lithium perchlorate was found to weigh 13.92425 grams. It was then heated to 300° for 5 hours more and lost 0.00025 gram. This loss was due to loss of oxygen, however, as shown by the fact that on adding dilute perchloric acid a pale yellow solution was obtained. This was again evaporated rapidly at about 210°. Gradually the temperature was raised to 240° and was

[1] Journ. Amer. Chem. Soc., 29, 815 (1907).

kept there until the excess of acid had been expelled and was then heated to 300° for 3 hours.   The weight was now 13.92419, or only 0.00006 less than the first weight.   As the heating had been brief, it was continued at about 300° for 4 hours more, when the weight was found to be 13.92416, essentially the same as before.   Upon being dissolved in very dilute perchloric acid no trace of yellow color was observable, showing that the substance this time had not been greatly decomposed.   Nevertheless, in order to test the matter yet again, the fused salt was dissolved in very dilute perchloric acid once more.

The water and perchloric acid were driven off as before, and the residual salt was dried 3.5 hours at 300°.   This time again the weight had changed only one-thirtieth of a milligram, being 13.92413 grams; and upon dissolving in dilute acid no trace of yellow color was to be perceived.   Thus the total loss in two evaporations amounted to only 0.00012 gram, or an average of about one-twentieth of a milligram for each evaporation.   This small loss is negligible, being only 1 part in 200,000 of the weight of material in question, and even this may be due to nothing more than a slightly greater loss of oxygen before the last weighing than before the first.   An accident prevented the determination of the amount of chloride in the fina sample.   In the carefully finished determinations given in the final table the amount of oxygen lost varied from 0.00009 gram to 0.00078 gram, or on the average about 0.0004 gram.   This is considerably more than the divergence between the weights given above, and therefore it is clear that the agreement noted above is as good as could be expected, and shows that no important amount of material is carried away with the stream of vapor and air during evaporation.

THE WEIGHING OF LITHIUM PERCHLORATE.

When perfectly neutral, lithium perchlorate is not in the least deliques-
cent in air of ordinary humidity; but the presence of a very little acid suf-
fices to make it so.   After several days' exposure the pure salt is still appar-
ently dry.   Nevertheless, great care was taken not to expose the contents
of the evaporating flask to the air.   The ground stoppers of the flask were
always kept closed, and although they were not quite as tight as those on
the weighing-bottles for the lithium chloride, they were evidently sufficient
for the purpose.

In order that the apparent weight of lithium perchlorate might be cor-
rected to a vacuum standard, the density was found by determining the
weight of toluene displaced by a known quantity of salt.   The toluene had
been dried over sodium and then distilled.   Its density at $25°$ referred to
water at $4°$ was found to be 0.8617.   Pure lithium perchlorate was fused
in a quartz crucible in a current of dry air, broken into coarse pieces, and
transferred to an Ostwald pycnometer, modified for use with solids.   Great
care was taken to remove all air-bubbles by shaking in a vacuum.   Table
7 records the results.

TABLE 7.—*Density of Lithium Perchlorate.*

Weight of $LiClO_4$ in vacuum (grams).	Weight displaced toluene in vacuum.	Density of $LiClO_4$ $25°/4°$.
5.2866	1.8757	2.4285
5.2866	1.8760	2.4283

The mean value is 2.428, and assuming the density of the weights as 8.3,
a correction of 0.0003501 gram was added to every apparent gram of lith-
ium perchlorate.

The weighing of the evaporating flask with its counterpoise proved to be
rather troublesome.   During the first few minutes on the balance the flask
lost somewhat in weight, frequently as much as 0.20 mg.; but eventually
the weight became constant.   Since both flasks showed this behavior it was
not a serious matter, for constancy with respect to one another was all
that was required.   After waiting until constancy had been reached, the
weight of the flask obtained after replacing it a second time upon the bal-
ance was usually within a few hundredths of a milligram of the first one.
The initial irregularity may have been due to absorbed moisture, but was
more probably due to slight temperature changes; for with so large a vessel
half a degree centigrade would cause this difference.   Hence the temper-
ature of the balance case and the flasks should not change appreciably
during the weighing; the more nearly this condition was realized, the more
accurate was the result.   A large pane of glass was placed between the
observer and the balance to prevent the heat of the body from reaching it.

IMPURITIES IN THE FUSED PERCHLORATE.

There could have been only four possible impurities in the salt (provided that the lithium chloride and the perchloric acid and water were pure and that the vessels were not attacked), namely, chloride, chlorate, hydroxide, and water. The tests for these will be discussed in order.

After the flask had been weighed, its contents were dissolved in 0.1 liter of water, and the chloride present in 25 milliliters was determined in the nephelometer. The amount was always small—usually less than 0.002 per cent—and the corresponding correction averaged about 0.4 mg. in 14.3 grams of perchlorate. Table 8 contains a statement of the amounts of chloride found in each of the final experiments and a correction which was applied to the final weight of lithium perchlorate containing these impurities in order to allow for the oxygen lost. It is evident that for every 0.425 mg. of lithium chloride found, 0.64 gram of oxygen must have been lost, these quantities being in proportion to the combining weights. In the last determination, involving over 22 grams of perchlorate, the correction was so small as to be practically negligible; and in only one or two cases, in which the heating had probably been somewhat too rapid, did the total correction amount to any serious quantity.

Traces of chlorate were always likely to be present with the chloride, and since the quantity was very small, it was most conveniently estimated nephelometrically after reduction with a solution of pure sulphur dioxide. This gave the total chloride, the amount corresponding to the chlorate being obtained by subtracting that previously found as chloride. The correction for chlorate was usually entirely negligible; its amount was determined in four cases, analyses 1, 2, 7, and 11. Only in the last of these cases, where the amount of lithium chloride found was unusually large, did the necessary correction equal one-twentieth of a milligram; it was usually less than one-thirtieth. As a rule the more chloride present, the greater was the amount of chlorate, although the proportionality was not exact. Because one-twentieth of a milligram was only 1 part in 300,000 of the weight of perchlorate in the case of experiment 11, and the amount present did not exceed this fraction in any of the other cases, the correction might have been entirely neglected without introducing appreciable error.

TABLE 8.

No. of experiment.	Weight of LiCl found.	Correction applied to weight of LiClO$_4$.
	mg.	*mg.*
7	0.13	+0.20
8	.50	+ .75
9	.16	+ .24
10	.21	+ .32
11	.52	+ .78
12	.06	+ .09

The formation of alkali was never observed, the solution of the perchlorate being always absolutely neutral to indicators. Even when the salt is *completely* decomposed into chloride, only a little oxide or hydroxide is formed, and in the specimens obtained in this work where only a trace of any kind of decomposition occurred, the amount of alkali must have been infinitesimal indeed.

Although it seemed probable that the salt dried under these conditions was perfectly anhydrous, the inference could only be verified by complete decomposition, as in the corresponding work of Richards and Forbes on silver nitrate. Lack of time has thus far prevented the completion of this final test, but a comparison of our work with the results of these authors indicates that the amount of water, if any, must be extremely small. They found certainly not over 0.001 per cent in silver nitrate dried one hour at 210°, while the lithium perchlorate was heated to 300° for 4 or 5 hours in perfectly dry air. The correction for 0.001 per cent of water in the perchlorate would raise the atomic weight of silver only 0.002.

Valuable information concerning the probably anhydrous nature of the salt, corroborating the above conclusions based on analogy, was actually obtained in four cases. During the progress of analysis 8 the lithium perchlorate was heated in the first place for 4 hours at 280°; 3 hours more at about the same temperature caused a further loss of only 0.19 mg., or 0.002 per cent. This loss, being much less than the weight of oxygen lost by the substance, may have been entirely due to the incipient decomposition. At any rate, even supposing the loss had been due to water, one might well infer that further heating could hardly expel more than 0.1 mg. additional. As will be seen, this inference was verified later. The ninth experiment was treated in dry air for 6 hours at 252°, a temperature at which the water would undoubtedly be expelled much less rapidly. Two and a half hours more at a temperature 30° higher caused the expulsion of about 0.2 mg., and yet 3 hours more at the same temperature caused a further loss of but little more than 0.1 mg. Thus only 0.003 per cent of the weight of the salt dried at 252° was lost by prolonged heating at 285°. Even this loss may have been due chiefly to oxygen, of which 0.24 mg. was shown to be lacking by the presence of 0.16 mg. of lithium chloride in the product.

In experiments 11 and 12 higher temperatures were used. After having been dried for 4.5 hours at 290° to 300°, the lithium perchlorate in this experiment weighed 17.84843 grams, and after further drying in a current of pure dry air for 3 hours at 300°, it weighed 17.84842, a loss of only 0.01 mg. It seemed unlikely that further heating even at this high temperature would cause any further loss of weight. The last experiment, No. 12, was the most conclusive of all. The salt was first dried for 5 hours at 280° and was found to weigh 22.58271 grams. After 3 hours further heating at 280°, 3 hours more at 300°, and a few minutes at 310°, the specimen weighed 22.58275, a slight *gain*, but one not exceeding a possible error of weighing.

Further heating for 1 hour at 300° caused an opposite change of only one-thirtieth of a milligram in this last salt. The weight accepted as the true one was 22.58273, and one can hardly believe that this substance still retained an appreciable amount of water. These weighings demonstrated not only the probable absence of water, but also the striking stability of the salt.

The four impurities which might possibly have come from the pure materials employed have thus been discussed in detail. It remains to consider the impurities which might have come from the vessels used and from the gases in contact with the fused materials.

The lithium chloride (forming the starting-point of the determination) was fused in a platinum boat. In most of the experiments this boat was weighed before and after the fusion, and was usually found to have lost but little. For example, in experiment 7 the loss was 0.02 mg., in experiment 8, 0.05 mg., and in experiments 9 and 10, taken together, only 0.01 mg. Thus in four experiments involving the fusion of over 18 grams of lithium chloride the total loss of weight was only 0.08 mg., or 0.0004 per cent of the weight of the lithium chloride. On the other hand, in the last experiment, No. 12, which was otherwise the best of all, the boat lost much more in weight, because in this case a new boat had been employed to accommodate the unusually large quantity of material. The loss was here 0.3 mg. There was every reason to believe, because in other cases the platinum was not attacked, that this excessive loss, amounting to 0.003 per cent of the lithium chloride, was due, at least in part, to iron volatilized from the boat during fusion at high temperature in hydrochloric acid. The boat had indeed been previously cleansed by treatment with ammonium chloride at high temperatures as usual, but apparently the cleansing had been insufficient. The mean weight of the boat was taken as the true one. Even the maximum error resulting from this choice amounts to only 1 part in 60,000 of the weight of lithium chloride, a quantity which seems often to represent the limit of accuracy in experimental work of this kind. On the whole, the evidence is that the boats were not sufficiently attacked to cause any important constant error in the series of results.

Turning now to the quartz flask, the only other receptacle used during the experiments, it was easy to prove that this was not appreciably attacked during the experiments. In three cases in which no regrinding of joints or alteration in tare weight had been necessary, the following successive tares of the evaporating flask were found: experiment 8, 0.00106; experiment 9, 0.00103; experiment 10, 0.00104. This practically proves that the flasks were not appreciably attacked by the acid lithium perchlorate at 300°. It is of course possible that the flasks gained from the fused mass a weight of lithium equal to the weight of silica dissolved, but this is unlikely, especially because the flasks to-day, after all the determinations, still appear perfectly clear and transparent, as they did at first.

Neither sodium chloride, silver chloride, nor silver nitrate were found in the previous investigations[1] to retain on fusion perceptible amounts of oxygen or nitrogen or argon, and, as the air and nitrogen passed over the lithium chloride and lithium perchlorate in the present experiments were both free from other gases, it is reasonable to infer that these salts also did not contain dissolved gas. The absence of hydrochloric acid from the lithium chloride which had been fused in the gas, and subsequently while fused heated in a current of pure nitrogen, was proved by complete neutrality of the dissolved product.

From these considerations it would appear that both the lithium chloride and lithium perchlorate were obtained in these experiments in a state of purity as great as is practicable in the present state of work of this kind, and therefore that the conclusions based upon the quantitative results are inferior to none.

THE RESULTS.

Table 9 contains the four preliminary results which were brought to a satisfactory conclusion. The third and sixth of this preliminary series were vitiated by known experimental errors, due to inexperience with the processes involved. No great accuracy is claimed for these results, but they serve to show that the process was one which was capable of exact work, and afforded the valuable training needed to carry out the six consecutive final experiments which followed. The lithium chloride used in these preliminary experiments was not perfectly pure, being of the same quality as that used in the preliminary experiments of the other series. In calculating the last two columns of the table below, values for the ratio LiCl : Ag were chosen which corresponded with the particular samples of slightly impure lithium chloride used in each case, namely, 0.39298 for experiments 1 and 2, and 0.39304 for experiments 4 and 5. Thus a large part of the error due to impurities in the lithium chloride was eliminated.

TABLE 9.—*Ratio of Oxygen to Silver; O_4: Ag.—Preliminary Series.*

No. of experiment.	Sample of salt.	Weight fused LiCl, vacuum.	Weight fused LiClO4, vacuum.	$\frac{4O}{LiCl}$	$\frac{4O}{Ag}$	Atomic weight of Ag.
1	O	4.24171	10.64596	1.50983	0.59333	107.87
2	O	5.09073	12.77683	1.50982	.59333	107.87
4	D	4.03587	10.12750	1.50957	.59324	107.88
5	D	5.19638	13 04021	1.50948	.59329	107.87
				1.50962	.59330	107.872

[1] Richards and Wells, Carnegie Institution of Washington Publication No. 28, 55, 60 (1905); Richards and Forbes, *ibid.*, 69, 55 (1907).

Thus the atomic weight of silver is shown by these preliminary results to be not far from 107.872. It is interesting to note that if Stas's value for the relation of lithium chloride to silver had been used in making the computation of these results, the atomic weight of silver recorded in the last column would have been 107.70. This value is quite impossible in view of results obtained in other ways, and serves to emphasize the grave error which unquestionably existed in Stas's work on lithium chloride.

These preliminary experiments having furnished an adequate preparation for the execution of an exact series of experiments, six syntheses yielding the results given in table 10 were made. The lithium chloride used in the determinations was preparation C, already used it previous work involving the comparison with silver. The advantage of using similar material in the two sets of experiments has already been emphasized. Every precaution was taken, and, although we feel that with the experience gained in these experiments, a yet more consistent series might be obtained, especially if somewhat larger quantities of material were used, nevertheless it is evident that this degree of accuracy will not be easy to exceed.

Table 10 explains itself. The weight of lithium perchlorate given was in each case obtained by adding to the actual weights (corrected to the vacuum standard) the corrections for chloride given in the last column of table 10, together with the vanishingly small corrections for chlorate mentioned just afterwards. In calculating the values given in the last and next to the last column, the ratio of lithium chloride to silver is assumed to be 0.392997 : 1, as previously stated at the conclusion of Part I. The experiments were consecutive; none was rejected.

TABLE 10.—*The Ratio of Oxygen to Silver; O_4:Ag.—Final Series.*

No. of experiment.	Weight fused LiCl, vacuum.	Corrected weight fused LiClO$_4$, vacuum.	$\dfrac{4O}{LiCl}$	$\dfrac{4O}{Ag}$	Atomic weight of silver.
7	5.09744	12.79265	1.50962	0.593276	107.876
8	4.20534	10.55416	1.50970	.593307	107.870
9	4.54205	11.39912	1.50969	.593302	107.871
10	4.45070	11.17008	1.50974	.593323	107.867
11	7.11167	17.84842	1.50974	.593323	107.867
12	8.99846	22.58273	1.50962	.593276	107.876
	*34.40566	86.34716	†1.50968	.593301	107.871

*Sum.   †Average.

Thus, according to this series of results, silver is 107.871, if oxygen is taken as 16.000 and the ratio of lithium chloride to silver is taken as 0.392997 : 1. A variation of 4 in the sixth decimal place of this latter ratio would cause a change of only 0.001 in the atomic weight of silver.

There seems to be no doubt that the ratio of lithium chloride to silver is not much more in error than this, and accordingly that the atomic weight of silver given by this series of results is free from error due to the work described in the first part of the present paper. The probable error of the final result, 107.871, according to the method of least three squares, is 0.003. The only possibility of serious uncertainty seems to lie in the possible retention of water by the fused lithium perchlorate. This would obviously tend to make the atomic weight of silver appear lower than it is. Accordingly we are disposed to believe that the value 107.871 represents the lower limit. The last analysis, made with the largest amount of material and showing the least decomposition, was probably the most satisfactory determination of all, and it will be noticed that in this case the value is somewhat higher than the average. If silver is 107.871, lithium becomes 6.939, essentially the same as if silver were 107.88. Chlorine is somewhat more affected by this difference in silver, sinking from 35.457 to 35.454.

Further determinations carried out as this last determination was, together with other experiments in which the possible presence of water remaining in the final substance should be sought in the manner used by Richards and Forbes in the case of silver nitrate, are needed to settle the third decimal place in the atomic weights of silver and chlorine beyond doubt, but the present investigation seems unquestionably to show that the atomic weights proposed by Stas, both for silver and for lithium, were much too high, and that the recent conclusion of many chemists that the value for silver is not far from 107.88 is entirely justified.

It is worthy of note that this investigation, taken together with that of Richards and Wells, gives values for chlorine, lithium, and silver referred to oxygen which are independent of all other work. That these values should agree so closely with other results obtained in such widely different ways is very reassuring as to the degree of precision now within reach.

SUMMARY.

This investigation consisted in a careful study of three ratios, namely, that of lithium chloride to silver chloride, that of lithium chloride to silver, and that of lithium chloride to lithium perchlorate. By means of the last two ratios, $O_4 : Ag$ was calculated, and new values were obtained in this entirely new way for the atomic weights of silver, lithium, and chlorine. In the process of this work new methods of purifying lithium salts, better than any preceding, were devised. Lithium chloride was fused in such a way as to show perfect neutrality to the most sensitive indicators, and was weighed in a strictly anhydrous condition. The preparation of perchloric acid also was subjected to rigid scrutiny, and this substance was made in a state of unusual purity. The sharpness of the end-point in the method used for determining the relation between silver and chlorine was much increased by cooling the solution to $0°$, in order to diminish the solubility of silver chloride. In other respects the methods of analysis developed in previous Harvard investigations were used in the determination of chlorine. A new precise method was devised for converting lithium chloride into lithium perchlorate, and its sources of error were carefully examined. 45.56877 grams of lithium chloride were found in 7 experiments to yield 154.0602 grams of silver chloride on complete precipitation; and in another series of 7 experiments partly independent from these 46.63197 grams of lithium chloride were found to need 118.65894 grams of silver for complete precipitation. In yet another series of 6 experiments, entirely independent, but using a similar preparation of lithium chloride, 34.40566 grams of this substance were converted into 86.34716 grams of lithium perchlorate. As an outcome of all these experiments, the atomic weight of lithium was found to be 6.939, and the atomic weight of silver 107.871, if oxygen is taken as 16.000.

The Harvard Determinations of Atomic Weights, between 1870 and 1910

BY

THEODORE W. RICHARDS

THE HARVARD DETERMINATIONS OF ATOMIC WEIGHTS, BETWEEN 1870 AND 1910.[1]

INTRODUCTION.

The history of the beginning and growth of a scientific investigation, or series of investigations, is always interesting, because it throws light upon the objects on account of which the work was undertaken, and gives a basis for more satisfactory judgment concerning the results. Therefore it is hoped that a useful result may come from the presentation of a brief history of the determinations of atomic weights which have been made in the Chemical Laboratory of Harvard College during the last forty years.

The Erving Professorship of Chemistry in Harvard University was founded in 1792, but the first Harvard professor who took an active interest in chemical research was Josiah Parsons Cooke, who was born in 1827 and died in 1894. His interest early turned to the philosophy of chemistry, and even in his younger days he was profoundly impressed by the significance and fundamental importance of the combining proportions of the elements. This is shown by his early paper([1])[2] on the so-called "triads" of Döbereiner and other relations between these numbers. In this publication he added somewhat to the knowledge of the subject, and his work has always been mentioned among those which led the way towards the more complete classification of de Chancourtois, Newlands, Mendeléef, and Lothar Meyer.

Cooke's subsequent work upon another subject, the crystalline compounds of zinc and antimony, caused him to think about these combining numbers from quite a different point of view. Irregularities in the composition of these crystals led him to study the atomic weight of antimony, a subject of interest with reference both to the system of the elements as a whole and to the then agitated question concerning the constancy of the atomic weights of the elements. The revision was particularly important because the work of Berzelius, Kessler, Schneider, Rose, Dexter, and Dumas failed to decide between the widely divergent values 120 and 122.5.

Cooke's revision of the atomic weight of antimony was the first extended work of the kind which had been attempted in America. With the help of several assistants and with great patience and care he synthesized sulphide of antimony and analyzed antimonious bromide, chloride, and iodide.[2]

In brief, his first method of procedure was as follows: He precipitated carefully prepared antimony by means of hydrogen sulphide in the presence of an excess of tartaric acid and in the absence of air; and the precipitate was collected by means of his process of reverse filtration. The antimonious sulphide was heated in hydrogen to a temperature of about 210°. In spite of much washing, it always contained traces of tartaric acid, but Cooke applied an approximate correction for this error. The corrected difference between the weight of the metal and that of the sulphide was taken as the weight of sulphur. Thus found, the percentage of sulphur in the sulphide varied from 28.42 to 28.60—an extent of variation which far exceeds the permissible limit nowadays. The errors are to be traced partly to partial sublimation of the antimony sulphide and partly to the impurities it must have taken from the solution, and the results therefore are of but little value; but the final outcome seems to agree with the work of Schneider in pointing to a value of about 120.

Seeking for more satisfactory light upon the subject, Professor Cooke next began the analysis of the chloride of antimony, repeating the work of Dumas and making many determinations of the composition of this substance. He found that, as a mean of many determinations, the chloride had a percentage composition of about 53.4 per cent of antimony and 46.6 per cent of chlorine. In his own words: "These new results, so far from throwing light upon the subject, only render the problem the more obscure and baffling." They correspond nearly to the value of 122.0 for the atomic weight of antimony, if chlorine is taken as 35.5. It occurred to him that perhaps the atomic weight of sulphur used in the earlier series might have been incorrect, and therefore he made approximate determinations of the relations between silver and sulphur by the reduction of argentic sulphide. The first series of experiments, carried out at a full-red heat, gave for the atomic weight of sulphur a value nearly 32.5, but he showed that these were vitiated by the sublimation of silver. The next series, carried on by reduction at a low-red heat, gave a better result, the values for sulphur ranging from 32.12 to 32.14 if silver is taken as 108. No evidence of sublimed silver was seen in this case.

Next, two experiments were made by reduction at a temperature below visible redness with still a lower result for sulphur, namely, 31.98; in these experiments it was certain that no silver was volatilized, but not certain that all the sulphide had been reduced. These experiments satisfied Cooke that Stas's atomic weight of sulphur was not far from correct; and that at any rate the value was probably between 32.0 and 32.1. Hence the

discrepancy in the atomic weight of antimony was not due to an error in sulphur.

Cooke therefore began the analysis of a new compound of antimony, the bromide, which he made with care and distilled repeatedly over pulverized antimony, and finally recrystallized from bisulphide of carbon. His fifteen determinations of bromine in this substance varied from 66.584 to 66.779, with a mean of 66.667 per cent, from which the atomic weight of antimony is easily calculated to be about 119.9. The results therefore confirm the analysis of the sulphide and not that of the chloride. Seven similar analyses of the iodide showed about the same range of error from 75.94 to 76.16 per cent of iodine, the mean being 76.05. This also corresponds very closely to the value 120 for antimony. Being convinced now that the low value 120 was the correct one for this atomic weight, Cooke turned back to the study of his chloride and proved that the discrepant results obtained were due to the invariable presence of oxychloride in this compound.

These experiments were all made before 1877. Two or three years afterwards Cooke, in answer to some objections of Kessler, made still others, confirming the earlier results and exhibiting a much more satisfactory concordance.([3]) In these experiments the percentage of bromine in antimony bromide was found to vary only between 66.662 and 66.670—a range comparing favorably with much of the work of Stas. This last work of Cooke, which points towards 119.86 as the atomic weight of antimony, if silver is taken as 107.88, is without much doubt the best work upon the subject. Incidentally it may be noted that all the atomic weights in this paper will be reduced to this standard, usually accepted to-day, although they are given, in the original papers referred to, a variety of other standards, such as Ag = 108, Ag = 107.66, Ag = 107.93. In the original publication of the present paper this was not done, partly from lack of time and partly because some doubt still existed at that time concerning the best value to choose.

A few years afterwards, under Cooke's direction, his nephew, Oliver W. Huntington, conducted a brief series of experiments upon the atomic weight of cadmium.([4]) This metal was chosen for study because its bromide may be very easily sublimed and therefore is capable of being treated in much the same way, with the same precautions, as Cooke's bromide of antimony. Because the latter had yielded such excellent results, Cooke hoped to apply all his methods here, as well as in a number of other cases. Moderate precautions were taken in preparing the substance, and the results of the sixteen experiments gave values ranging from 112.14 to 112.27 for the atomic weight of cadmium, if silver equals 107.88. The mean was 112.2; and this furnished the value of the atomic weight of cadmium which seemed the most probable for a number of years, until the qualitative work of Bucher and the quantitative work of Baxter and Hines

showed that it was somewhat too low. The latter investigation, which gives without question the nearest approach to the true value, will be discussed further on in this paper.

In Cooke's next research I had the good fortune to be associated with him, having been attracted to Harvard not only by the high reputation of the ancient university, but also because of Cooke's well-known interest in the philosophy of chemistry, and because of the eminence of his colleagues, Professors Wolcott Gibbs, C. L. Jackson and H. B. Hill. After a year's preparatory work I had become Professor Cooke's assistant and began, under his direction, an elaborate research upon the atomic weight of oxygen.[6]

HYDROGEN AND OXYGEN.

The previous determinations of the atomic weight of oxygen had been made chiefly by a method undesirably complex. The weight of oxygen had been determined by the loss of weight of copper oxide during its reduction to copper, and that of the hydrogen by the difference between the weight of water formed and this weight of oxygen. Thus all the error of the process was accumulated upon the measurement of the hydrogen, the smallest amount to be determined. In order to improve this method we sought to weigh the hydrogen directly in large glass globes, containing 5 liters, which were filled with this gas, prepared in a state of the highest purity. The globes were counterbalanced by similar globes of equal exterior volume, and it seemed reasonably certain that the weighings were accurate to within 0.1 mg. or 0.03 per cent. The hydrogen was prepared in three different ways: in the first place from hydrochloric acid with the help of pure zinc, the acid having been scrupulously freed from air; in the next place electrolytically, and in the third place by the action of aluminium upon potassic hydroxide solution.

After having been weighed with all possible precautions, the gas was burned by means of carefully prepared oxide of copper, which had been dried at a moderate red heat; and the water was collected and weighed. Thus in this case the oxygen, not the hydrogen, was found by difference. In this way fifteen determinations were made, five with each kind of hydrogen, and the values found agreed within a reasonable limit of error. The highest result was 15.977 and the lowest was 15.937, the average being 15.953 (±0.002) for the atomic weight of oxygen. The total weight of water formed amounted to over 55 grams.

After the conclusion of these experiments it was pointed out to the experimenters by Lord Rayleigh that they, in common with all previous investigators of gases, including Regnault himself, had committed an error in assuming that the weight of a gas is equal to the difference between the indicated weighing of the globe full and that of the globe empty. When the globe is exhausted the pressure of the atmosphere diminishes its volume and therefore its buoyancy. Hence the weight of the gas within it appears

to be less than it really is, because the globe is too heavy when empty. As our globe was still intact, nothing was easier than to find the amount of this correction and apply it. It was found as a matter of fact that our 5-liter globe was diminished in volume by as much as 1.66 c.c., corresponding to almost 2 mg. of displaced air.([8]) Hence this quantity had to be added to each of the weights of hydrogen, a proceeding which had the effect of diminishing the corrected atomic weight of oxygen to 15.869. If oxygen equals 16.000, hydrogen equals 1.0082.

There seemed to be no reason to doubt the precision of this final result, although it was at the time unique; no one had believed that the atomic weight of oxygen could be so low as this. The subsequent magnificent work of E. W. Morley and later of W. A. Noyes has shown that, as a matter of fact, our value is not far from the correct one, being indeed nearer to the truth than any which had preceded it. Clarke's most recent recalculation has pointed to the result for hydrogen as 1.0078, differing from ours by only 0.0004. It is interesting to note that several of the single determinations in the Harvard series gave results as low as this.

COPPER.

During this work upon the atomic weight of oxygen it was necessary to study very carefully the preparation of the oxide of copper. This substance was found to exhibit so many peculiarities as to cause doubt concerning the accepted atomic weight of copper, which depended partly upon a determination of the composition of this compound. The doubt was emphasized by the results on the electrochemical equivalent of copper, presented to the British Association by W. N. Shaw during the summer of 1886; and with the approval of Professor Cooke I proceeded with the redetermination of the atomic weight of this element,([5]) using the occasional long intervals in the oxygen research for this purpose.

As a new method for the determination of the atomic weight of copper, the simple precipitation of silver by copper was thought to give promise of good results. It was found that, unless the solution of silver nitrate is at its freezing-point, some basic salt of copper is formed during the reaction, and accordingly an insufficient amount of silver is obtained. At the freezing-point, however, this irregularity seemed to be wholly eliminated and the results were very consistent and apparently satisfactory. It was found, as a matter of fact, that the atomic weight of copper must be as high as 63.57 if silver is 107.88, instead of the usually accepted value 63.31.([7]) This great discrepancy suggested further investigation.

The second method adopted for the determination of the atomic weight of copper was also a new one. On account of the easy analysis of bromides, bromide of copper was chosen as the typical compound for analysis, but this substance could not be prepared in a dry state without loss of bromine. It was crystallized from an aqueous solution, and the pure crystals were

then dissolved, to form a standard solution.   Of this solution weighed por-
tions were analyzed for copper by electrolysis, and other weighed portions
for bromine, in the usual manner—determining both the silver needed for
the precipitation and the argentic bromide formed.   The results of both
these methods of analysis agreed almost exactly with the results obtained
by the direct precipitation of silver by copper, giving respectively the values
63.575 and 63.579 for the atomic weight of copper, with a very small range
of experimental error,([9]) if silver is taken as 107.88.

These two investigations, which had used copper from sources as widely
different as Germany and Michigan, seemed to fix the atomic weight of
the element, but they did not show in what respect the earlier investi-
gations (of Hampe in particular) had been in error.   Hampe had analyzed
cupric sulphate which he supposed to be anhydrous and cupric oxide which
he believed to be pure, and these two compounds had brought almost
identical values (about 63.31) for the atomic weight, and therefore fur-
nished an argument almost as strong as the newer determinations.   Before
the atomic weight of copper could be decided, it was therefore necessary
to discover the possible reason for the discrepancy.   With this end in view
yet a new investigation was started on this subject, an investigation in
which these two compounds were subjected to a more searching analysis
than had ever before been attempted.([10])   By convincing experimental
argument it was shown that the cupric sulphate which Hampe supposed to
be anhydrous really contained over 0.1 per cent of water.   Thus it con-
tained less copper than the pure compound, and the atomic weight of the
element appeared to be lower than the true value.   It was shown also that
the oxide of copper prepared exactly according to the method of Hampe
contained several hundredths of 1 per cent of nitrogen derived from the
nitric acid with which the copper had been combined—for the oxide was
made by the ignition of the nitrate.   By a curious coincidence this im-
purity in the oxide was almost exactly enough to produce the same effect
upon the atomic weight of copper calculated from its erroneous composi-
tion, as had been the impurity in the cupric sulphate.   Therefore the
reason for the error in both of Hampe's series of experiments was demon-
strated conclusively.

Not content, however, with such destructive experimentation, the author
proceeded to obtain new and correct data from both these compounds.
The sulphate was in the first place dried thoroughly at a temperature
(360°) sufficient to drive out almost all of the water which Hampe had
left in the salt at 240°.   It was then dissolved in water and electrolyzed,
all the copper being precipitated.   The acid solution was all collected and
exactly neutralized with carefully weighed amounts of sodium carbonate.
Thus was obtained the ratio $Na_2CO_3 : Cu$.   There was inevitably some
uncertainty as to whether the sodium carbonate was thoroughly dried, and

in the light of our present knowledge it seems probable that the salt must have contained some residual traces of water or other impurity, perhaps occluded air, since the substance was very finely divided.

The basis for such an inference is at least twofold. In the first place, it is notoriously difficult to dry thoroughly a solid substance without fusion, and fusion was impossible in this case. In the second place, the recalculation of the results with the most recent value for the atomic weight of sodium seems to indicate that the sodium carbonate was too heavy, because the atomic weight of copper computed from the result (namely, 63.54) comes out less than it was found to be according to any of the other methods employed. Moreover, the ratio between the weight of sodium carbonate and that of the sodium sulphate made from it do not accord with our modern knowledge concerning the atomic weights of carbon and sulphur. This possibility was dimly recognized even at that time and, in order to make assurance double sure, the solution of sodium sulphate which was formed was carefully evaporated and the salt was fused at so high a temperature as to make the expulsion of water certain. Because the result accorded with the atomic weights accepted at that time, considerable confidence was placed in the sodium carbonate results, but this confidence was partly misplaced. Thus was obtained the valuable further ratio $Na_2SO_4 : Cu$. One may likewise compute from these data the less significant ratios $(CuSO_4 - Cu) : Cu$; also $Na_2CO_3 : (CuSO_4 - SO_4)$, and several others which need not be mentioned here.

As the atomic weights of the elements concerned have been revised since that time, all these results need recalculation. Of the various ratios the most accurate, for reasons given above, is probably the ratio $Na_2SO_4 : Cu$. In the final series 4.94652 grams of the former substance were found to be equivalent to 2.21306 grams of the latter, from which, if $Na_2SO_4 = 142.06$, $Cu = 63.557$, only slightly different from the value previously found by an entirely different method. The other ratios, of very doubtful value for many reasons, range from 63.44 to 63.64, the range being somewhat greater than it was with the old values of the atomic weights, but the average of the most trustworthy results indicating essentially the same value $Cu = 63.60$ if $Ag = 107.93$, or in the modern standard $Cu = 63.57$ if $Ag = 107.88$.

Those who desire to know the details may consult the excellent discussion by Branner in Abegg's Handbook, **2, 1,** 459 to 468. Here the recalculation to the modern standard is given in full.

In addition to this work on bromide and sulphate, the oxide of copper also was analyzed with great care, the nitrogen present being carefully estimated. The corrected results from this compound gave the figure 63.604, but little higher than the others. Thus the protracted investigation, which lasted four years, left no doubt as to the probable value of the atomic weight of copper and entirely overthrew all the earlier work.

BARIUM.

During the progress of the work just described an attempt had been made also to determine the sulphuric acid in the copper sulphate by means of barium, but it was very soon obvious that the atomic weight of barium was much less accurately known than that of copper at that time, and that the precipitation involved numerous uncertainties. Therefore this method was abandoned. With the practice acquired in the extended work upon copper the author ventured to attack this new problem which had just come under his notice, namely, the atomic weight of barium, although this constant had previously been studied by men as great as Dumas and Marignac. The early determinations of the atomic weight of barium varied from 135 to 139, and it was obvious that new work was needed.

The first step was, as usual, the choice of the compound to be analyzed; and this choice was finally settled in favor of the bromide, which is easily prepared in a pure state, is capable of being dried without decomposition, and may be analyzed with great ease. Because it seemed inadvisable to attempt the determination of the barium in the salt, it was necessary to make very sure that all the water was expelled, the barium being found by subtracting the weight of the bromine from the weight of the salt. Therefore especial experiments were instituted in order to find out the temperature and the precautions needed. In some cases where a trace of hydroxide was formed it was found possible to determine this slight impurity with the help of phenol-phthalein and thus correct for it.

Great care was taken in preparing the salt for analysis to purify it with the utmost nicety, especially from strontium and calcium, and blank tests were instituted in order to show the efficiency of the methods which were employed. The salt used for the analysis was prepared in seven different ways, and the different specimens were found to be essentially the same in composition.

The silver used was prepared as in the previous case, reverting to the method of Stas, except that after fusion it was cooled both before and during its solidification in a reducing flame, instead of being fused in the oxy-hydrogen blow-pipe and poured into water. The object of this precaution is evident. Stas's silver was undoubtedly contaminated with oxygen, and the fusing in a reducing atmosphere was expected to remove this gas. Many years afterwards this hope was justified by the investigation of Richards and Wells, as will be seen.

The bromine was determined both by weighing the argentic bromide containing it and by finding the silver necessary to produce this precipitate.

The results for the atomic weight were almost exactly the same according to both methods. For silver, 107.88, and bromine, 79.916, the values were respectively 137.367 and 137.362. The greatest variation from the mean was 0.05.

While this work was in progress the chloride of barium also was being subjected to analysis in a series of experiments even more extended and careful than those concerning the bromide. In this case also it was a matter of very great importance to dry the salt thoroughly, and much time was spent in determining its properties upon heating. Some of the salt was dried in the air without fusion; some was fused in the air; some was fused in hydrochloric acid, and some was not fused at all, but the amount of anhydrous salt present was found by making a separate determination of the water in part of the same sample. In this way the weight of barium chloride corresponding to a definite weight of the crystallized salt was found with the greatest precision, and a sufficient basis was found for determining the precise weight of the anhydrous salt to be analyzed.

At first an attempt was made to determine the ratio $BaCl_2 : BaSO_4$, but the purity of even the best barium sulphate was found to be too uncertain to form the basis of any reliable conclusions. Accordingly, the determination of the halogen by combination with silver was again undertaken.

This analysis was by no means so simple as in the case of the bromide. Stas in his early work ignored entirely the solubility of silver chloride, although this is sufficient to cause a very serious defect in any work pretending to accuracy. In his later work Stas devised methods for determining the end-point of the reaction of dissolved silver upon a soluble chloride, showing that by adding a sufficient excess of silver all the halogen could be precipitated. It seemed desirable, nevertheless, to confirm this knowledge, and accordingly new methods for accomplishing the end in question were devised and were used to verify Stas's methods, which were found to be approximately correct. Slight errors were found in later investigations, as will be shown. The silver also was prepared in a variety of ways and the greatest variation shown between the purity of the different samples was 1 in 20,000. The outcome of the work gave a value for barium about one unit in the second decimal place higher than that obtained from the bromide when calculated with the value for chlorine then accepted. At the time the reason for this difference was not discovered, but will be explained later. Recalculated with the new atomic weights of silver and chlorine, the results were 137.365 and 137.346 respectively. It seems reasonably certain that the atomic weight of barium must be not far from the mean of the four closely agreeing values, namely, 137.36.

In this case, as in the case of copper, not only were new results obtained, but also the reasons for the deviations in the old ones were made clear. It was shown that these errors depended, in the case of both Dumas and Marignac, as well as in most all other cases, upon the lack of knowledge of the solubility of silver chloride in water, as well as upon the retention of water by baric chloride. It should be noted that among the earlier investigators Turner, the Englishman, obtained results which were very nearly accurate as long ago as 1829.

STRONTIUM.

Next among the atomic weights, strontium was undertaken, because it was obvious that the same errors which entered into the determinations of the atomic weight of barium were at work here also, and it was deemed especially desirable to obtain accurate values for those elements which formed well-marked series in the periodic system. Among such elements it seems reasonable to suppose that a possible numerical relation is most likely to be found.

Strontium was studied in the same way as barium, both as the bromide and chloride. The bromide was investigated first. As before, great care was taken to prepare the salt in a state of purity, for obviously the success of the work depended entirely upon this matter. An advance was made in the analyses in that the salt was fused in dilute hydrobromic-acid gas, diluting the gas with nitrogen together with a slight admixture of hydrogen to prevent the formation of bromine and the corrosion of the platinum boat containing the salt. Moreover, in this analysis the first form of the so-called bottling apparatus, so much used for other salts subsequently, was devised. This apparatus will be explained shortly. The device made it possible to inclose the dried salt without allowing the access of the least trace of water. Therefore one of the most important difficulties in the other cases was overcome. In this investigation also for the first time the nephelometer—an instrument which made possible the detection of faint traces of precipitate suspended in liquids([45])—was used.

The atomic weight of strontium calculated from the ratio of argentic bromide to strontium bromide was 87.660 and from the relation of silver to strontium bromide was 87.666, the mean being 87.663, if silver is taken as 107.93. With the modern atomic weight of silver the mean becomes 87.623.

Curiously enough the results with chloride obtained shortly afterwards did not agree with these values, but yielded the value 87.693, if chlorine was taken with Stas as 35.455, a difference which was clearly beyond the experimental error. At the time no explanation for this anomaly was apparent, and accordingly the results from the chloride, which seemed to be less trustworthy on account of the solubility of silver chloride, were not published for ten years. Later it will be shown that the error lay not in the Harvard results, but rather in the accepted value of Stas's atomic weight of chlorine. This matter will be discussed in detail when that atomic weight is discussed.

ZINC.

The next atomic weight which received consideration at Harvard was that of zinc. The choice of this metal for investigation was made chiefly because the detection of nitrogen in copper oxide led to the conclusion that this gas might be contained also in the oxide of zinc, which had been used by others for determining the atomic weight of the metal. The problem was assigned to a student, E. F. Rogers, and he found, as a matter of fact, that many oxides obtained from nitrates contained more or less nitrogen.[12] Zinc oxide was especially noticeable in this respect. Accordingly the atomic weight of this metal was studied in another way. Again the bromide was chosen, for reasons already mentioned; and it was found possible by sublimation and distillation to prepare samples of bromide of zinc which were essentially free from water. As usual, great care was taken to prepare all the materials in a state of great purity. In this way it was found, as was expected, that the atomic weight of zinc was considerably higher than the previously accepted value, the new number being 65.37 instead of 65.22, if silver is taken as 107.88. Afterwards Morse and Burton, determining the nitrogen in their zinc oxide according to our suggestion, corrected their results for the oxide to 65.44, so that there seems to be no doubt that the value obtained from the bromide was about correct. Once more not only had new figures been proposed, but the reason for the errors of the old ones had been made clear.

MAGNESIUM.

The determination of the atomic weight of zinc naturally suggested that of magnesium, not only because the metals are in many respects similar and belong to the same general group, but also because the same methods had been used for determining their atomic weights, namely, the conversion of the metal into the oxide by solution in nitric acid and ignition of the nitrate. It having been proved by the Harvard experimenters that such oxide of magnesium always contains nitrogen, obviously the quantitative results ignoring this impurity could claim no great authority.

In the case of magnesium the atomic weight was found most easily by reference to the chloride, because this salt can be prepared in a pure state by ignition of the magnesium ammonium chloride more easily than any other.[18] The ignition was carried on in a stream of dry air containing a small amount of hydrochloric acid. The presence of hydrochloric acid in the fused salt was not feared, because in the research upon barium its absence had been quantitatively proved in barium chloride made in the same way. The investigation was conducted with the assistance of H. G. Parker, an expert analyst, and it was with his help that the bottling apparatus was improved in such a way as even more effectually to shut out the possibility of the absorption of water from the atmosphere.

A description of the apparatus is perhaps apropos. The hard-glass tube used to contain the platinum boat with the magnesium ammonium chloride was ground with a long tapering joint directly into the wider tube used to contain the weighing bottle. This wider tube had a bulb or pocket blown upon one side of it to receive the stopper of the weighing bottle. The arrangement thus allowed the boat to be pushed past the stopper directly through the ignition tube into the bottle. Afterwards the stopper could be pushed into place with a rod provided for the purpose. During this fitting of the stopper a current of dry air sweeping through the apparatus prevented the introduction of any moisture. The drawn-out end of the ignition tube was protected by a drying tube, containing phosphorus pentoxide, until the moment when the weighing tube was finally closed. Subsequently the weighing tube was easily removed, placed in the desiccator, and weighed at leisure. This apparatus is illustrated in the preceding paper of Richards and Willard. It was thus possible to prepare pure magnesium chloride which showed no trace of oxide or basic salt and could not have absorbed water during its cooling. Weighed portions of this salt were analyzed for chloride, both by determining the silver needed and by weighing the precipitated argentic chloride in the manner already used for the barium. Several series of results were executed. From the ratio of the silver chloride to magnesium chloride the value, 24.335, may be computed for the atomic weight of magnesium, assuming silver to be 107.88 and chlorine 35.457, whereas by finding the necessary amount of silver for precipitation, the atomic weight was found to be 24.318. The last series was much the most reliable, the extremes being only between 24.316 and 24.320. The silver used was prepared with great care and was probably fully as pure as that used in the case of barium.

It must be borne in mind that in the original paper these atomic weights were calculated with Stas's atomic weight of chlorine, which was afterwards discovered to be erroneous, namely, 35.455. In the calculation given above the modern values are used, in conformity with the practice adopted throughout this present paper.

NICKEL AND COBALT.

The possible identity of the atomic weights of nickel and cobalt had always been an interesting and somewhat puzzling problem from the standpoint of the periodic system, or indeed from any philosophical conception of the reason for definite numbers. If the atomic weights are ultimately connected with the properties of material, it is scarcely conceivable that two atomic weights should have identical values. Such a belief would lead to the necessity of assuming a kind of internal isomerism within the ultimate atoms of the elements in question. The problem was one which

had always interested me; and with the experience gained in the preceding investigations, it seemed as if the matter might be once for all settled by a more accurate investigation of these atomic weights than any which had been attempted before at that time. Accordingly, in 1896, an investigation was begun simultaneously upon both of them, with the collaboration of two very capable advanced students, Allerton S. Cushman working with nickel ([19, 23]) and Gregory P. Baxter with cobalt.([20, 24])

The bromides of these two elements were chosen as the best starting-point, for obvious reasons. The first part of the investigation involved the study of the properties of these substances and the means of preparing them in a pure state. It was found that this preparation was possible. After the pure metal and pure bromine had been made, the substances were easily combined and the product could be sublimed in a stream of hydro-bromic acid and nitrogen gases with great success. The bottling arrangement devised for use with magnesium was found amply sufficient to guard the somewhat hydroscopic substances from moisture during weighing, and in this way both salts were prepared and weighed with accuracy.

The analysis was more complete than any of the preceding, because in this case it was possible to determine the bromine with reference to silver and silver bromide on the one hand and the metallic nickel and cobalt by reduction of the salts on the other. Thus complete analyses were possible, a much desired outcome, unattainable in the other cases of bromides. The halogen determinations were carried on in aqueous solution in the usual way and offered no new features. The reduction in hydrogen was accomplished at a comparatively low temperature, using other specimens of salt. Both salts were found to be contaminated with about 0.1 per cent of sodium bromide taken from the porcelain tube during sublimation. For this impurity corrections were duly applied.

This work yielded five ratios for the atomic weight of cobalt and nickel, the results of which are given below, on the assumption that Ag = 107.88.

	Ni.	Co.
From the ratio 2AgBr : the bromide.	58.676	58.968
From the ratio 2Ag : the bromide...	58.677	58.960
From the ratio metal : the bromide..	58.682	58.971
From the ratio silver bromide : metal.	58.679	58.967
From the ratio 2Ag : metal.........	58.680	58.965
Mean......................	58.679	58.966¾

Against this array of concordant data the earlier determinations have no weight. Thus the two atomic weights are seen to be really different.

Although it seemed reasonably certain that these values represented the true ones for both the metals, it seemed worth while to carry the matter

yet further, in the case of one of them, in order to bring into consideration some other compound. Accordingly Baxter and the author continued the work upon cobalt, studying the chloride[25]. At this time, which was before the invention of vessels of fused quartz, it was not possible to obtain the substance wholly free from alkali and silica, and accordingly the results were not conclusive. They yielded, by the reduction of the salt in hydrogen, a somewhat but not greatly higher value, which certainly seemed to be the upper limit. Later work by Baxter, using pure quartz vessels, improved upon these results, and wholly confirmed the work on the bromide, as will be shown.[57]

The oxide also was analyzed by the two experimenters in 1899.[25] In this case it was found very difficult to prepare the substance in a perfectly pure state. The substance was obtained by the ignition of cobaltic oxide, but there was good reason to believe that not all the excess of oxygen was expelled by the ignition. The mean of three results was in this case 58.954, a result almost as much on the lower side of the true value as the other work with the chloride was on the upper side. As the errors in each case would lead one to expect such differences, the values, although not satisfactory by themselves, could only be looked upon as confirmation of the results upon the bromide, and we left the subject with complete confidence.

<div align="center">IRON.</div>

The next problem concerning atomic weights undertaken in the laboratory was of a similar nature, namely, the revision of the atomic weight of iron.[28] In this case the ferric oxide, being so stable a compound, seemed to offer the best starting-point. The oxide was made from pure ferric nitrate many times recrystallized, and after weighing was reduced in a current of hydrogen. This method of making pure iron has since been adopted by many experimenters as the best. The results ranged from 55.870 to 55.890 for the atomic weight of iron, and although they were not wholly conclusive, they seemed more so than any of the previous determinations. The work has since been verified by Baxter working alone according to the method used for cobalt bromide. This further work is recounted on a following page.

ELECTROCHEMICAL EQUIVALENTS OF COPPER AND SILVER.

Simultaneously with this work another of quite a different nature was in progress. The question as to whether the chemical combining proportions agree exactly with the electrolytic equivalents was one which had never been satisfactorily settled. According to the atomic hypothesis there was every reason to believe they should agree, but the matter was one which could not be settled without actual experiment. The electrochemical

equivalent thus offers an entirely new method of approach with regard to the combining proportions; and with this in mind (as well as with the hope of simplifying and making more certain the determination of electricity by the coulometer or voltameter) I sought, with the efficient help of E. Collins and G. W. Heimrod, to compare the weight of silver and copper precipitated from their salts by an identical current. Basing our work upon previous work of Rayleigh, Gray, Shaw, Vanni, etc., we succeeded in showing that the amount of copper precipitated is a function of the size of the cathode plate. This irregularity is due to the solution of the metal during the act of deposition, to form a small percentage of cuprous sulphate in the solution. By extrapolating to a plate of no area at all we could approximately correct for this dissolving tendency, and in this way found for the atomic weight of copper a value which was much nearer the chemical value than that yielded by any previous electrical work.[27]

The copper question having been thus settled, we turned our attention to the deposition of silver and succeeded in proving that under certain well-defined conditions, namely, the conditions when the freshly concentrated liquid around the anode was allowed to flow directly upon the cathode, too high results were obtained for the silver deposit. The error through this cause varied greatly with the temperature, the rate of agitation of the solution, and the forms of the vessels. We prevented it by inclosing the anode in a porous cup. If this correction is applied, as we found it for the particular case in hand, the atomic weight of copper referred to silver must lie in the neighborhood of 63.58 if silver is taken as 107.88—a result which confirms with reasonable precision the value 63.57, found for the atomic weight of copper by the chemical methods of eight years before.

Later, the precipitation of silver was studied much more in detail under varying circumstances and the former results were confirmed and amplified.[37]

With the help of W. N. Stull it was shown also that precisely the same quantity of silver is precipitated from a solution of silver nitrate in fused sodium and potassium nitrates at 250° C. as from an aqueous solution at 20°, when the proper correction has been made for traces of solvent included in the crystals.[41] This is the most striking confirmation of the exact and universal precision of Faraday's law which has ever been offered.

With the help of B. S. Lacy it was shown further that electrostenolytic growths between the cathode and anode have no effect upon the weight of silver deposited on the cathode.[50]

Thus the atomic weights are shown to represent numerical relations which persist under widely differing conditions.

CALCIUM.

During the years 1897 to 1899 an investigation upon the atomic weight of calcium was begun in the Chemical Laboratory of Harvard College—in some respects more elaborate than any previous similar research there conducted.   This research has not yet been finished, but a brief report of five preliminary results was made to the American Association for the Advancement of Science in August, 1899.([39])   The investigation was undertaken in order to supplement the work upon barium and strontium, by the same experimenter.

In spite of the common occurrence of the element calcium, its atomic weight had been investigated only in a partial and incomplete manner. The chief work upon the subject has consisted of the quantitative ignition of calcium carbonate, and it seemed important to obtain also data of a radically different kind.

Accordingly the present series of determinations consisted of the analysis of calcium chloride, the silver chloride obtained from a known weight of the anhydrous salt being collected and weighed with care.

The first problem to be solved was the preparation of pure calcium chloride.   Preliminary experiments showed that calcium nitrate is the best salt to use for recrystallization, because of the rapid variation of its solubility with the temperature, and because of the fact that the corresponding salts of magnesium, strontium, and barium do not crystallize out with it. Two portions of marble were used as the starting-point; one came from Rutland, Vermont, U. S. A., while the other was a specimen of the purest Italian marble taken from a ship which had just arrived at the port of Boston.   The Rutland marble was converted into the nitrate, and from this specimen, after preliminary purification with lime, etc., two samples were prepared, one having been carefully recrystallized ten times and the other twenty times.   The single specimen of pure nitrate from the Italian marble was recrystallized fifteen times, thus being comparable with the average of the American samples, in case any difference between them might exist.

The metal in each of these specimens was precipitated as carbonate by the purest ammonium carbonate, and then converted into chloride.   After four recrystallizations the chloride was dried, ignited in a platinum boat inclosed in a porcelain tube in a stream of hydrochloric-acid gas to render a possible trace of silica insoluble, dissolved, filtered, and crystallized twice more.   As in all recent Harvard work, of course, platinum vessels were used throughout, and every precaution was taken.

The three samples of material which had thus been made ready were dried for analysis by prolonged ignition and final fusion at a bright red heat in a porcelain tube.   The hydrochloric-acid gas, which had been added to the nitrogen in the tube to prevent loss of chlorine, was then wholly

displaced by the inert gas, and when the apparatus was nearly cold this was driven out by dry air. After having been transferred to the stoppered weighing-bottle by means of the convenient automatic bottling apparatus so much used at Harvard, it was weighed and analyzed. The correction for the solubility of the silver chloride was determined much as in the case of barium chloride, several years before.

The results show that the three samples of calcium chloride (which were wholly neutral to methyl orange) were essentially identical. Hence neither a change in the source of the material nor repeated fractionation causes any variation in the atomic weight.

The ratio $2AgCl:CaCl_2$ alone was determined. The results for calcium varied only between 40.081 and 40.090, the average being 40.086, if argentic chloride is taken as 143.337. This value for the atomic weight of calcium was somewhat higher than the accepted value, but it is not so high as the value 40.142 since obtained by Hinrichsen, who was not cognizant of the Harvard work. The value 40.09 may for the present be taken as the most probable value for the atomic weight; the bromide of calcium is now being studied at Harvard with the hope of obtaining further knowledge.

URANIUM.

Even before the discovery of radioactivity great interest was attached to uranium on account of its unique position at the end of the system of atomic weights. It occurred to me that possibly this element, with its very high atomic weight, might exhibit any irregularities in its quantitative behavior not shown by the others; and this curiosity was heightened by Becquerel's brilliant discovery; the study of uranium was therefore begun in 1897 with the assistance of a skilful student, B. S. Merigold.[36]

The investigation extended over four years. Many compounds were investigated, at first with unsatisfactory results, the manifold valencies of the element greatly complicating the problem. This complexity, which so often causes uranium preparations to be contaminated by the presence of traces in other stages of oxidation, is probably the reason for the widely discrepant results of various experimenters. After much trouble and thought, the tetrabromide was selected as the typical compound to be analyzed, partly because the non-existence of the pentabromide makes it not very hard to prepare the tetrabromide in a pure state, and partly because of the ease of its analysis. Various difficulties, too numerous to mention, were overcome; but finally a series of fairly satisfactory results was obtained pointing to a value of 238.42 for the constant in question, if silver is taken as 107.88. This value is probably more accurate than earlier work; but the atomic weight is one which will bear further study.

While the research was in progress the astounding work of the Curies and Rutherford appeared, and caused us to speculate yet further concerning the significance of our results. It should be stated in this connection that our

material had been recrystallized so many times as to be essentially non-radioactive at the time of the experiments; but several months afterwards it was found to have developed radioactivity in normal amount, as Rutherford found in his own specimens.

CÆSIUM.

Next, the atomic weight of cæsium was undertaken,([42]) because of the opportunity offered by the kindness of Prof. H. L. Wells, of Yale University, to work with large quantities of his exceptionally pure material. E. H. Archibald, a careful and persevering student who has since done excellent work alone, assisted in this research.

The first part of this investigation used essentially the quantitative methods which had been adopted in other cases. The chloride and bromide of cæsium were prepared in a perfectly pure state by crystallization, as cæsium dichloriodide and tribromide, respectively. One of the specimens of chloride was made from material which had thus been recrystallized twenty-five times, but it was found to be essentially similar to that which had been crystallized only three times. Hence there seemed to be no doubt as to the purity of the material. 100 grams of silver were found to be equivalent to 155.964 grams of cæsium chloride, and 100 grams of silver chloride were found to be equivalent to 117.398 grams of cæsium chloride. These figures correspond to values for the atomic weights of cæsium = 132.800 and 132.817, respectively, if silver is taken as 107.88 and chlorine as 35.457. The corresponding values from the bromide were 132.819 and 132.820. The average of these figures, 132.814, may be taken as the true value.

Preliminary results obtained by the decomposition of cæsium nitrate with silica, and of potassium nitrate with silica, seemed to confirm these values, but the newly found values for the atomic weights of potassium and nitrogen disturb the consistency of the results. Therefore it is probable that the method is at fault, and demands further study.

In the course of a parallel series of analyses of potassium chloride, it became evident that the atomic weight of potassium computed from the precipitation of silver chloride (39.137) was somewhat lower than that obtained by the direct comparison with metallic silver (39.141), both being calculated on the old basis $AgCl = 143.385$. The best determinations with cæsium had shown the same phenomenon to a less degree. The reason for this discrepancy was not then apparent.

The recurrence of differences of this kind brought to mind once more the discrepancy in the case of strontium between the results with the chloride and the bromide, as well as the somewhat less manifest discrepancy in the case of barium. Nevertheless, because in the case of cæsium there was no great difference between the results from the chloride and the bromide when calculated on the old basis, the explanation still seemed to be

far away; and the matter was kept in mind with the intention of searching for a possible explanation in future work. As will be seen, it was shown conclusively later that all these discrepancies were due to the erroneous value for chlorine used as a standard of reference by Stas.

SODIUM AND CHLORINE.

The next atomic weights undertaken in the laboratory were those of the very common elements sodium and chlorine.([48]) These two, which had supposedly been determined by Stas with the utmost accuracy, were not taken up lightly or without a full sense of the grave significance of the task. There could be no object in studying these elements unless the work of Stas could be improved upon, and the assumption that it was possible to improve upon this work involved no small daring.

The immediate cause of the attack was as follows: In the process of a series of investigations upon the transition temperatures of hydrated salts for the purpose of obtaining new exact points in thermometry, a sample of very pure sodium bromide was obtained. This substance, by undergoing transition at a perfectly definite point, gave evidence of great purity. Thus it seemed worth while to make a few analyses of its composition; the subject was taken up with the expert collaboration of R. C. Wells, who had done the work upon the transition temperature. Assuming the usual atomic weights of silver and bromine, namely, 107.93 and 79.955, the atomic weight of sodium appeared to be 23.008, a value almost 0.2 per cent lower than that of Stas.

Such a discrepancy as this was not to be passed over lightly; it indicated either an unknown constant impurity in the sodic bromide and hence a possible error in the transition temperature, or else a flaw in the classical work of Stas. When the first cause of disagreement had been carefully sought in vain, the second was pursued. Thus a physico-chemical investigation, demanding great purity of material, led to a quantitative research of unexpected magnitude; and, in turn, this quantitative investigation depended continually upon physico-chemical methods and considerations. To this new work was brought all the recent knowledge of physico-chemical processes acquired since the days of Stas, and it was found that this knowledge was able in many cases to make possible a real advance. More carefully than ever before, the fundamental details of each step of the process were studied.

In brief, the chief errors which we found in the work of Stas upon sodium chloride were as follows: In the first place, he dropped the *solid chloride* into his solutions of silver nitrate, thereby causing occlusion of the sodium chloride by the precipitate. In the next place, his sodic chloride was prepared in such a way as probably to contain traces of platinum and silica. Finally, he read the end-point of each analysis in a slightly incorrect man-

ner. All these errors, which appear in much of his earlier work also, tend to make the atomic weight of sodium too high.

In his preparations of silver, his chief error lay in impurities, both solid and gaseous, in the silver. It had been prepared in the first place with sufficient care, but his method of fusing it and preparing for weighing must have introduced over 0.01 per cent of impurity. We found that silver containing oxygen could be freed wholly from this gas only by fusing in an atmosphere of hydrogen, while supported on a crucible or boat of pure lime.

In the present investigation all Stas's errors and many others were avoided. The salt and silver were obtained from many sources and purified in many ways. Every step of the analytical work was tested in order to prove its trustworthiness. Every substance to be weighed was finally fused in a vacuum in order to eliminate occluded gases or vapors. The details are too complicated for description here. In the course of the work the following points were developed:

1. Sodic chloride, obtained from many sources and purified in many ways, always gave the same equivalent weight.

2. Fusion in vacuum of this salt already fused in air caused no change in this equivalent weight.

3. Argentic chloride precipitated from aqueous solution always occludes traces of other substances present, and those traces can not always be eliminated.([44]) Very dilute solutions must hence be used in the precipitation. The conditions governing the occlusion and release of these impurities were minutely studied.

4. A careful study of the solubility of argentic chloride was made and the precautions necessary in using the nephelometer in the estimation of traces of chloride and silver were ascertained.

5. It was shown that fused argentic chloride probably contains traces of dissolved air, but not enough to affect essentially its weight, since subsequent fusion in vacuum caused no appreciable loss of weight.

The investigation consisted of a very careful quantitative study of three ratios, namely, $AgCl:NaCl$; $Ag:NaCl$; and $Ag:AgCl$. In the present review it will suffice to give the sum total of the quantitative results.

In the consecutive determinations, carried out with the greatest care, 44.5274 grams of sodic chloride yielded 109.1897 grams of fused argentic chloride. In twelve entirely separate determinations, with all the possible refinements, 49.5007 grams of sodium chloride were found to be equivalent to 91.3543 grams of the purest silver.

If silver is, as usual, assumed to be 107.93 and chlorine 35.455, the values for the atomic weight of sodium computed from these two results are not identical. Their difference, 0.010, seemed after long research to be due to no error in them; hence an error must exist in the molecular weight of silver chloride used in one of the calculations. This conclusion led to a

prolonged investigation of the amount of this substance which could be made from a known amount of silver, and involved a searching study of methods of preparing pure silver.

Two entirely different methods were used for effecting the synthesis of the chloride, with the final result that 82.6689 grams of the purest silver yielded in ten determinations a sum total of 109.8395 grams of argentic chloride. This corresponds to an atomic weight of chlorine of 35.473 if silver is taken as 107.93. Applying this value to the sodium work, the atomic weight of this metal becomes 23.006 from one series and 23.009 from the other. The mean of these values, 23.008, agrees closely with the provisional value found from the bromide, and may be accepted as the true atomic weight of sodium, until better data are obtained. This is about 0.18 per cent less than the value 23.050 found by Stas and then accepted by the world. When reduced to the modern standard, Ag = 107.88, the atomic weight of sodium becomes 22.995 and that of chlorine 35.457.

These new values, and the improved methods which led to them, inevitably play havoc with the second decimal place in most of the other atomic weights, including that of silver. While the early Harvard researches stand this innovation better than most others, the fact that once or twice (especially in the case of cæsium) Stas's value for chlorine had been verified, shows that his errors were not wholly eliminated. Indeed, this research on sodium and chlorine is probably the first Harvard research in which Stas's precision had been exceeded.

On the other hand, this discovery of Stas's undoubted error in the case of chlorine—a discovery which was immediately confirmed by Baxter's[52] and Köthner and Aeuer's comparison of chlorine and iodine—explained at once the reason for the discrepancies already noted between the results obtained from the various metallic chlorides and their corresponding bromides. As the atomic weight of chlorine which was used in the calculation was too small, the residual value ascribed to the metal was too large. On applying the new atomic weight of chlorine to the results, especially to the results upon strontium, it was found that values at least as low as those obtained from the bromides were obtained. Thus in the investigation ten years previous 100 parts of silver had been found to correspond to 73.477 parts of strontium chloride. With the new atomic weight of chlorine this gives the value Sr = 87.621, whereas that from the bromide was 87.623.[49]

Of course, as the equivalent of a metal grows more and more nearly equal to that of silver, the error produced by the comparison of its chloride with silver chloride becomes less and less. Therefore this discrepancy was not so apparent in the case of metals with larger equivalents, such as cæsium.

While this work was in progress Dr. Baxter, who had in the meantime been appointed instructor and later assistant professor at Harvard, was

undertaking the study of other atomic weights, more or less connected with these.   He used for the most part the methods which had been worked out at Harvard, but added to these results his own experience.

FURTHER STUDY OF IRON.

Baxter's first independent work of this kind consisted of a continuation of the revision of the atomic weight of iron.[45]   Very pure metallic iron was heated in a porcelain tube, in a current of pure, dry nitrogen and hydro-bromic-acid gases, at a temperature high enough to sublime the ferrous bromide formed.   The sublimed salt was then heated in a weighed platinum boat in a current of the same gases until moisture had been expelled and all ferric salt had been decomposed.   Finally the boat was transferred to a weighing-bottle without exposure to moisture and weighed.   After the oxidation of the salt to the ferric condition by means of a dilute solution of an equivalent amount of potassic dichromate, the bromine was determined by weighing the silver bromide.   In two analyses the proper amount of the purest silver was dissolved in nitric acid and added to the solution of the bromide.   By testing the resulting solution with silver nitrate and hydro-bromic acid solutions, in a nephelometer, it was shown that no excess of either bromine or silver was present.   As in the cases of nickel and cobalt, an impurity of sodic bromide, which had been extracted from the porcelain tubes, was found in the salt.   When corrected for the presence of this sodic bromide, the final result for the atomic weight of iron becomes 55.845. Although the previous analyses of ferric oxide by Richards and Baxter had yielded the somewhat higher value 55.883, the fact that in the ferric oxide-work it was found difficult to secure even apparently complete reduction, and the fact that bromides are in general so well adapted for exact analysis, leads one to place more reliance on the lower value.   In fact, very recent experiments with ferrous bromide, not yet published, confirm the earlier bromide analyses.

IODINE.

Subsequently Baxter undertook the revision of the atomic weight of iodine,[47] being stimulated thereto by the recent papers of Scott and Ladenburg.   He used several methods, the first being the synthesis of silver iodide from a definite amount of silver.   Weighed amounts of the purest silver were dissolved in nitric acid and precipitated with a slight excess of purified ammonium iodide in ammoniacal solution which was subsequently made acid with nitric acid, the silver iodide being collected on a Gooch crucible and weighed.   Several different samples of iodine, from which the ammonium iodide was made, were purified from chlorine, bro-mine, and cyanogen, by repeated fractional distillation from an iodide and

by boiling in the form of hydriodic acid solution. A search for a possible similar element of higher atomic weight than iodine was conducted by repeating four times the process of converting the iodine into hydriodic acid by means of hydrogen sulphide, and setting free about one-half the iodine with potassic permanganate. In the fourth repetition of the process the remaining iodine was set free in four fractions by introducing the permanganate in small successive portions. The first fraction would probably contain nearly all of any unknown element of atomic weight higher than that of iodine occurring in the original substance, if such an element exists. The samples nevertheless all gave essentially the same results, $i.$ $e.$, I $=$ 126.914.

As a check on the value obtained by synthesis of silver iodide three analyses were completed in which the direct ratio between silver and iodine was found. The iodine was weighed in a glass-stoppered weighing-tube into which it had been sublimed in a current of dry air. It was dissolved in sulphurous acid and added to a solution of very nearly its equivalent of silver. Then the excess of silver or iodine was found in a nephelometer and a deficiency of either was made up by adding dilute solutions of silver nitrate or hydriodic acid. The average atomic weight of iodine computed from this work, 126.918, was almost the same as that found by synthesis of silver iodide.

Finally, the ratio between iodine and chlorine was found by heating weighed quantities of pure silver iodide, contained in quartz crucibles, in a current of dry chlorine.

Further investigation upon the subject of the atomic weight of iodine was carried out by Baxter in the following year.[52] Silver iodide was converted into silver bromide and silver chloride in succession. Moreover, weighed portions of iodine and weighed portions of silver were combined, yielding a complete synthesis of silver iodide. On the average the weight of the product exactly equaled the weights of the two component elements. This paper was much more complete and thorough than the preceding, and in calculating the results the new atomic weight of chlorine was used and found wholly consistent with the new data. Baxter's final value for the atomic weight of iodine is 126.926 if Ag $=$ 107.88, a result which seems without question to be the most trustworthy and to leave little to be desired.

There can be no doubt, in view of these determinations, in conjunction with those of Köthner and Aeuer and of the others already mentioned, that Stas was really in error almost as seriously in the case of iodine as in the case of sodium. Stas's percentage error here was about 0.1 per cent, a quantity which makes a greater actual difference in the case of iodine than the 0.2 per cent error in the case of sodium.

CADMIUM.

Next Baxter undertook the revision of the atomic weight of cadmium, because it seemed highly desirable to verify the earlier work and to put at rest the doubts concerning its value which had been raised by the work of others in other places. The investigation was undertaken with the help of M. A. Hines, and showed conclusively that Huntington's value was too low instead of being too high, as many had supposed.[51] Both the chloride and the bromide were analyzed, the materials being of course prepared with the greatest care. Ammonium cadmium chloride was heated in a stream of hydrochloric acid until the ammonium chloride was expelled, as in the case already described of the atomic weight of magnesium, and the chlorine in this salt was determined according to the usual Harvard methods. Both silver and silver chloride were weighed; and from these two series were obtained the values Cd = 112.424 and 112.410, respectively, if silver is equal to 107.88.

This investigation upon the atomic weight of cadmium by analysis of the chloride was shortly after continued by the analysis of cadmium bromide, carried out by the same experimenters with the help of H. L. Frevert.[53]

Weighed portions of the very carefully prepared pure bromide, after fusion in a current of nitrogen and hydrobromic-acid gases, were first titrated against weighed portions of the purest silver. Subsequently the precipitated silver bromide was collected and weighed, with all the usual precautions. The results from the two series were identical, the average atomic weight of cadmium calculated from the two series being 112.415.

Phosphorus pentoxide had been used as a drying agent for hydrochloric-acid gas in the previous research upon cadmium chloride; and because this substance might have contaminated the gas with compounds of phosphorus, further analyses of cadmium chloride were carried out, in which the salt was fused in hydrochloric acid which had been dried with sulphuric acid only. The results of these analyses were 112.417 for the atomic weight of cadmium—an outcome which, by agreeing exactly with the earlier work, showed that no error could have been introduced there by the contamination of the hydrochloric acid by oxychloride of phosphorus.

The wholly concordant results from both chloride and bromide proved that the atomic weight of cadmium must be very near 112.42.

BROMINE.

The recent work showing that Stas was in error about both chlorine and iodine suggested that bromine also might have suffered at his hands. The previous Harvard analyses made this seem unlikely; but for certainty Baxter undertook new syntheses of silver bromide from weighed quantities of the purest silver, by dissolving the metal in nitric acid, precipitating silver bromide with an excess of ammonium bromide, and collecting the silver bromide upon a Gooch crucible.[55]

Bromine was freed from chlorine by two distillations with bromides in the case of sample I, three distillations in the case of sample II, and four in the case of samples III, IV, and V. The bromide had been made each time from a portion of the bromine itself.

In order to verify the value obtained by the synthesis of silver bromide, the ratio of silver bromide to silver chloride was found by heating weighed quantities of pure silver bromide, contained in quartz crucibles, in a current of dry chlorine. The result of thirty-one experiments gave, as the atomic weight of bromine, the value 79.916, if Ag = 107.88. Thus Stas's value reduced to the new silver basis (79.918), as well as the earlier Harvard results (79.917)([47]), were essentially correct. There is as yet no certain explanation why Stas found the true value when working with silver which was undoubtedly impure; but the most probable one is that his bromine contained iodine; just as it was probable that his iodine contained bromine. The earlier Harvard results were made with purer silver; hence one concludes that the bromine used in them must have been purer also.

MANGANESE.

Next Baxter and Hines began the study of the atomic weight of manganese by the analysis of bromide and chloride.([56]) In two cases the manganese was freed from other metals by often repeated crystallization of potassium permanganate. After reduction with sulphur dioxide, both samples were converted into bromide through the nitrate and carbonate. The pure bromide, which was made from carbonate reprecipitated from the nitrate, was several times recrystallized in quartz and then in platinum vessels. Two other samples were obtained from commercial pyrolusite and manganous sulphate respectively. Purification was effected by fractionation with hydrogen sulphide and sodium hydroxide, and by crystallization of manganous nitrate and bromide.

The bromide was fused, weighed, and analyzed according to the usual Harvard methods; and the several samples were found to give consistent results. The highest individual result was 54.942 and the lowest 54.917; but the most of the thirty-one analyses came very near to the mean 54.932.

In continuing the research manganous chloride was made, dehydrated by fusion in hydrochloric acid, and then analyzed in essentially the same way as the bromide; it gave almost exactly the same value, 54.933, if Cl = 35.457 and Ag = 107.88.

The close agreement of the averages of the various series and of the averages from the different samples of material leaves little doubt that the atomic weight of manganese lies very near the value 54.93 (Ag = 107.880). This value confirms the work of Dumas, Marignac, Dewar and Scott, and Weeren.

FURTHER STUDY OF COBALT.

The invention of fused-quartz vessels having added a new possibility of preparing substances in a pure state, Baxter sought with the help of F. B. Coffin to revise the earlier incomplete work on the chloride of cobalt.[57]

As usual, several samples were made.   First, purpureo-cobalt chloride was prepared in a pure state by repeated solution in ammonia in platinum vessels and precipitation with hydrochloric acid in quartz dishes; and the final product was converted into cobaltous and ammonium chlorides by careful heating.   Again, pure electrolytic cobalt was dissolved in hydrochloric acid, and the chloride was recrystallized in platinum.

Weighed portions of these preparations of pure chloride, after being heated in pure dry hydrochloric-acid gas to expel ammonium chloride and moisture, were analyzed in the usual double fashion with results which wholly confirmed the earlier work with the bromide,[20, 24] in which the atomic weight of cobalt had been found to be 58.968.   The new value is the essentially identical number 58.970, if chlorine equals 35.457 and silver equals 107.88.

LEAD.

Although the atomic weight of lead was determined by Stas, considerable uncertainty as to the correctness of his work apparently existed even in his own mind; and because determinations of this constant by other experimenters are somewhat discordant, Baxter, with the assistance of J. H. Wilson, undertook the analysis of lead chloride.[64]

Two specimens of carefully purified lead nitrate were precipitated as chloride and the lead chloride was recrystallized from hydrochloric acid several times.   The chloride was prepared for weighing by fusion in hydrochloric acid, and the analysis of the salt for chlorine was effected as in other similar cases.   The atomic weight of lead found in this way, 207.09 (Ag = 107.88), is two-tenths of a unit higher than that obtained by Stas.

ARSENIC.

A redetermination of the atomic weight of arsenic was undertaken by Baxter in collaboration with F. B. Coffin.[66]   Silver arsenate was chosen for analysis, since the percentage of silver in this salt can be determined with great precision by methods described in previous researches.   The salt was prepared by precipitation from solutions of soluble arsenates, and after thorough washing was dried for analysis by being heated in a current of pure dry air at 250°.   Then, after being weighed, it was analyzed either by heating in a quartz tube in a current of hydrochloric-acid gas until all arsenic was expelled, or by solution in nitric acid and precipitation with either hydrochloric or hydrobromic acid.   All three methods gave essentially identical results.

The proportion of water in the dried salt was found by fusing weighed amounts of the salt in a current of dry air and collecting the water set free in a weighed phosphorus pentoxide tube.   After applying a small correction found by blank experiments with the apparatus, the proportion of water was determined to be 0.0056 per cent.

It was found that material precipitated with trisodium arsenate contains a slightly larger percentage of silver than that formed with disodium ammonium arsenate, triammonium arsenate, or disodium arsenate.   On account of the distinctly basic nature of trisodium arsenate it is probable that the silver salt made from it contains basic impurity.   Hence results from this material were rejected.

The percentage of silver in the pure absolutely anhydrous silver arsenate was calculated to be 69.9116 whence the atomic weight of arsenic is 74.96 if silver is taken as 107.88.

SILVER.

The analysis of iodine pentoxide furnishes one of the most direct methods of finding the atomic weight of silver referred to oxygen, since by multiplying the ratio $2Ag:I_2O_5$, by the ratio $I:Ag$ the per cent of iodine in the pentoxide is found, and thence the ratio $2Ag:5O$.   This research was undertaken by Baxter, assisted by G. S. Tilley.([67])   Iodic acid, made by the action of pure fuming nitric acid upon the purest iodine in vessels of fused quartz, was purified by crystallization in quartz vessels.   After careful dehydration in a current of pure dry air at 240° C., the resulting iodine pentoxide was weighed.   Then it was dissolved in water, reduced in dilute nitric acid solution by means of hydrazine, and finally precipitated in very dilute solution with a few tenths of a milligram excess of silver.   This excess of silver was determined gravimetrically after evaporation of the entire filtrate to small volume.   In a preliminary series of experiments by Tilley the ratio of silver to pentoxide was found to be 0.646210 and in a second series by Baxter the ratio obtained was 0.646215.

Even after drying at 240° C. the iodine pentoxide was found to contain traces of moisture, which was estimated by completely decomposing the iodine pentoxide in a current of dry air and collecting the water in a weighed phosphorus pentoxide tube.   The proportion of moisture found in this way was 0.0023 per cent.

From the gain in weight when air was admitted to an exhausted tube containing a weighed amount of iodine pentoxide it was shown that no appreciable amount of air is adsorbed on the surface of the pentoxide.

Using the ratio of silver to iodine already found by Baxter, 0.849943, and applying a correction for moisture, the atomic weight of silver is found to be 107.850 referred to oxygen 16.000.

Unfortunately the method is very sensitive to an error in the ratio of silver to iodine—a given percentage error in this ratio producing one three times as large in the atomic weight of silver referred to oxygen.   Hence the

final outcome of this analysis must remain in some doubt until the ratio of silver to iodine can be redetermined with even greater accuracy than before. Further work upon silver, some of it by means of a method free from any objection of this kind, will be described on subsequent pages of this book.

CHROMIUM.

With the assistance of M. A. Hines and E. Mueller, Baxter undertook the revision of the atomic weight of chromium by the analysis of silver chromate, the procedure being very similar to that used with silver arsenate.[68] The chromate was precipitated from dilute solutions of potassium or ammonium chromate with silver nitrate. After washing and drying at 225° C., weighed amounts of salt were dissolved in nitric acid and reduced with either sulphurous acid or hydrazine sulphate. Subsequently the silver in the solution was estimated as chloride or bromide. The salt was found to have retained 0.0144 per cent of moisture. Different samples of silver chromate were found to possess essentially the same composition and to contain (after allowance for the trace of water) 65.0333 per cent of silver. If silver has the atomic weight 107.88, that of chromium is then 52.008.

The atomic weight of chromium was further investigated by Baxter and R. H. Jesse, jr., by the analysis of silver dichromate, which was purified by crystallization from dilute nitric acid.[69] After being dried at 200° C., it was dissolved and reduced, and the silver content was determined. Traces of nitric acid and moisture retained by the salt were determined, and corrections applied.

Allowing for these corrections, really pure silver dichromate was calculated to contain 49.9692 per cent of silver, whence the atomic weight of chromium is 52.014, if the atomic weight of silver is 107.88. The average of this value and that from silver chromate may be taken as 52.01, which represents the most probable value for the atomic weight of this element.

PHOSPHORUS.

In an investigation very similar to that upon the atomic weight of arsenic, Baxter and Grinnell Jones determined the percentage of silver in silver phosphate.[70] Four specimens of silver phosphate, prepared from disodium ammonium phosphate, disodium phosphate, and sodium ammonium hydrogen phosphate, were dried at 400° C. and weighed, and after solution in nitric acid the silver was precipitated as bromide or chloride. It was found experimentally that the salt retained less than 0.0005 per cent of moisture when dried at 400°C., and that it does not adsorb air.

The different samples of silver phosphate all had essentially the same composition and contained 77.300 per cent of silver, whence the atomic weight of phosphorus is 31.03, if silver possesses the atomic weight 107.88.

To this list should be added neodymium, now being investigated by Baxter and H. C. Chapin. They find the value 144.27 for this constant, in a careful research soon to be published.

This closes the present record of Baxter's extended investigations. The more recent of these papers are being collected for publication by the Carnegie Institution of Washington. Turning back chronologically a few years, the review of my own work may now be continued.

POTASSIUM.

The atomic weight of potassium is a chemical constant of unusual interest and significance; standing, as it does, in the middle of the series of five atomic weights of the most electropositive metals—substances which exhibit in a highly marked degree both marked similarity and progressive change in their properties—this number must be of unusual importance in the search for that undiscovered mathematical relationship which undoubtedly exists between these constants. Moreover, the atomic weight of potassium is essentially bound up with the atomic weight of oxygen and chlorine and silver—this group having formed a fundamental basis in the calculation of nearly all the other atomic weights.

The recent investigation upon the atomic weight of sodium showed conclusively that Stas's work, upon which rested the earlier knowledge, was somewhat at fault. In view of this fact it seemed not impossible that his work upon potassium also might be somewhat erroneous, and hence I decided to take up the study of the atomic weight of this element also. For this purpose the collaboration of two able analysts was secured, namely, of A. Staehler and E. Mueller; the former investigated potassium chloride,[58] the latter, potassium bromide.[59]

The chloride was made in several ways. Potassium nitrate was found very advantageous as a means of freeing the metal from other similar metals by recrystallization, and the nitrate was converted into the chloride by precipitation with hydrochloric acid. Repeated treatment brought the salt to perfect purity.

The details of the other methods need not be recounted. It is enough to say that all the samples were found to be quantitatively identical. All the other substances needed were likewise purified with the greatest care, although the details of the process were so similar to those of the foregoing discussion of sodium that it is not worth while to describe them again. Several minor improvements were introduced in the methods; and those seeking to carry out an investigation of this sort should consult the detailed publication. Platinum sponge instead of asbestos was used in the Gooch crucibles for collecting the precipitate, which had been used in all the other Harvard cases from that of barium chloride onward.

The individual results for the atomic weight ranged from 39.094 to 39,099, the two ratios AgCl:Cl and Ag:KCl giving essentially identical averages, pointing to 39.096 as the atomic weight of potassium, if silver is taken as 107.88.

The work upon potassium bromide was in many respects similar, but varied from the preceding in a number of particulars. In the first place, it having been found that potassium oxalate is as satisfactory as the nitrate for purifying potassium salts from other metals, the initial substance was recrystallized in this way. This was converted into bromide by two methods, partly by direct treatment with pure bromine in vessels of pure quartz, and partly by electrolysis, yielding an amalgam which was then converted into the hydroxide and neutralized with very pure hydrobromic acid. The salt was fused before weighing, as in the other cases, in pure dry nitrogen, and in general it was treated as the other cases at Harvard. Here again two ratios were found, namely, $AgBr:KBr$ and $Ag:KBr$. The fifteen results varied between 39.093 and 39.100, with the average of 39.096, having a probable error of less than 1 in the last place. The exact coincidence of these two investigations involving four ratios gives overwhelming evidence in favor of the new atomic weight, which is nearly 0.1 per cent lower than that of Stas.

SULPHUR AND SILVER.

During the last few years increasing testimony has been brought forward upon many sides, especially by Guye, pointing to the possible error in Stas's atomic weight of silver, 107.93. One method of approaching the subject would naturally be through silver sulphate and silver sulphide, and as a part of the investigation upon these two substances the study of the former was taken up at Harvard with the collaboration of an able advanced student, Grinnell Jones.[61] It was found that with special precautions silver sulphate could be prepared in a pure state and fused to expel water without essential decomposition. It was found, moreover, that the sulphate could be completely converted into silver chloride by heating in a current of hydrochloric-acid gas, but that it could not be converted wholly into chloride by the precipitation from aqueous solution. Accordingly the molecular weight of silver sulphate was found with great precision by igniting (in a small weighed bulb tube of fused quartz through which a current of hydrochloric-acid gas was passing) accurately weighed portions of silver sulphate, until the decomposition was proved to be complete. In this way it was found that 100 parts of silver sulphate yielded 91.933 parts of silver chloride, the individual numbers ranging between 91.929 and 91.937. The greatest deviation was thus $\frac{1}{23000}$ from the mean. If silver is taken as 107.93 and chlorine as 35.473, sulphur must equal 32.113; this is a very improbable value for sulphur. On the other hand, the assumption of a value for silver as low as 107.88 and chlorine correspondingly 35.457, gives sulphur = 32.069. This is a much more probable value for sulphur. Thus, as far as one can tell without more precise knowledge of the composition of the silver sulphide, the lower atomic weight of silver seems to be indicated by this work.

NITROGEN AND SILVER.

Simultaneously with this work a somewhat similar investigation upon silver nitrate was in progress. This substance is peculiarly interesting because it is an essential link in the chain of reasoning, pointing to the low atomic weight of silver. The work of Rayleigh and Guye and others upon this matter is too well known to need detailed review; but some have doubted Stas's work upon silver nitrate, and it seemed essential to put the composition of this substance upon a firmer basis.

In repeating this work I sought to exceed in accuracy any chemical work which had ever up to that time been published, and was so fortunate as to secure an able experimenter, G. S. Forbes, to carry it on.[60] The process was unusually interesting on account of the complications which surround this comparatively simple synthesis. The method consists, first, of weighing pure silver, converting in the usual manner into nitrate, and evaporating the solution to dryness; nothing could be simpler, apparently.

The essentials for success are first, the preparation of pure silver; secondly, the conversion of all this into nitrate without loss; and thirdly, the proof that the nitrate thus formed is perfectly pure. Of these three problems the first, namely, the preparation of pure silver, has so often been described that further words describing it are unnecessary. The second problem was not a new one; it is comparatively easy to prevent loss of silver during the solution and evaporation, which were conducted in flasks of pure quartz. The real difficulty lay in the last problem after the quantitative work had been finished. Was the dry fused salt thus produced really pure nitrate? Whatever it was, there could be no doubt that it had attained a position of perfect constancy, for the six results exhibited a wholly satisfactory agreement, as the following figures show: 100,000 parts of silver were found in six experiments to yield 157.481, 157.480, 157.480, 157.480, 157.481, 157.480 parts of the nitrate.

In order to settle the question concerning the purity of the product, it was examined with the greatest care for dissolved gases, for nitrous and nitric acids, for ammonia, and finally for water. Not only were these tests made with the greatest care, but also minimal traces of these various substances were tested in the same way to be sure that the tests were adequate, By far the greatest trouble was found in the attempt to find water in the salt; this was carried out by completely decomposing the substance and then absorbing all the oxygen in the issuing gases by means of copper reduced by carbon monoxide, and catching the water in phosphorus pentoxide. By means of long-protracted experiments far more difficult than the original synthesis, it was proved that there were no dissolved gases, nitric acid, or nitrous acid present, that the amount of ammonia was less than $\frac{1}{2000}$ of 1 per cent, and that the amount of water was less than $\frac{1}{1000}$ of 1 per cent. The observed value 157.480 could therefore be corrected to

157.479, with confidence that it could now probably not be more than one unit in the last place in error. The result is of great interest, for it proves beyond reasonable doubt that if nitrogen has, as is probable, as low an atomic weight as 14.01, silver must really have the atomic weight 107.88, which has been assumed throughout this article, instead of 107.93, as Stas supposed. This difference seems small, and yet one must remember that it corresponds to 0.5 mg. in a gram, a quantity within the reach of a beginner with any common analytical balance.

The last-mentioned work is one of the most accurate among the list of published determinations from the Harvard Chemical Laboratory. Indeed, it is hard to see where a defect could have crept into the various processes concerned, or into the final conclusions.

In connection with this investigation another may be briefly discussed, although, strictly speaking, it ought not to be classed among the Harvard researches on atomic weights, because it was made in Germany. During the summer of 1907, the author, at that time Visiting Harvard Professor at the University of Berlin, continued there the exact analysis of ammonium chloride, preliminary steps toward which had already been taken at Harvard during the preceding year.([65]) At this time the methods suitable for the study of this compound were worked out with the help of two able collaborators, Paul Köthner and Erich Tiede, guided by the experience already gained at Harvard in this direction. The usual methods needed several modifications of detail, partly because of the difficulty of obtaining ammonium chloride in a strictly typical condition free from excess of either ammonia or acid, and partly because of the fact that the salt on cooling changes its crystalline form, becomes permeated with minute interstices, and thus renders doubtful the correction to vacuum. In order to avoid the error from the first cause, the substance was sublimed first in a current of ammonia and finally in a vacuum; and the difficulty due to the change of bulk during the cooling of the salt before weighing was obviated by adapting the bottling apparatus for use in a vacuum. This ammonium chloride, being entirely protected from air or any other gas during its final weighing in an evacuated, hermetically closed weighing-bottle, could be weighed with the utmost precision.

By the time these details had been worked out, the senior member of the partnership had been obliged by his duties in Harvard University to return to America, and the actual analyses were accordingly made by the two others in his absence. The investigation was published under all three names, because whereas the two younger investigators alone carried out the analyses, the American was chiefly responsible for the methods. Although probably not giving the last word upon the subject, this work was without doubt superior in several respects to any previous investigation concerning ammonium chloride; first, as to the purity of the material; secondly, as to the choice of conditions for subliming the salt; and thirdly, as to the accu-

racy of the analyses. Ammonium salt had been prepared in such ways as to render the presence of carbon compounds very unlikely, and doubly sublimed in the way already described; the analysis was executed with all the care used in recent work in Harvard University, taking due account of the solubility of silver chloride.

Fifteen analyses were made. Of these the first two preliminary determinations were vitiated by inexperience and had no significance. One other, the sixth, was likewise rejected because of known fault. In the remaining twelve analyses 19.5795 grams of ammonium chloride, weighed in vacuum, yielded by processes already described in the cases of sodium and potassium 52.4620 grams of silver chloride. If the atomic weight of silver is taken as 107.88, chlorine as 35.457, and hydrogen as 1.0076, the atomic weight of nitrogen, computed from these results, becomes 14.0077. Among these analyses the fifth, eighth, and tenth are less reliable than the others, because of the small amounts of material used in them. The rejection of these doubtful experiments scarcely affects the result, however. In the nine most trustworthy analyses 16.7613 grams of ammonium chloride yielded 44.9104 of silver chloride, corresponding to nitrogen = 14.0084 (on the assumptions already indicated). This result was accepted as probably representing the true value. The various samples of ammonium chloride prepared in different ways gave essentially the same results.

It is interesting to note that these figures, in connection with the recent work carried out with the assistance of Wells and Forbes, together with the modern value for the atomic weight of hydrogen, provide a basis for calculating the atomic weights of silver, chlorine, and nitrogen entirely independent of any other investigations.

The calculation is very simply carried out as follows:

$$\frac{AgCl}{Ag} = a \tag{1}$$

$$\frac{NH_4Cl}{AgCl} = b \tag{2}$$

$$\frac{AgNO_3}{Ag} = c \tag{3}$$

The three atomic weights supposed to be unknown may be designated as follows:

$$Ag = x \qquad Cl = y \qquad N = z$$

From the work of Morley hydrogen may be taken as 1.0076, if oxygen = 16. Substituting these values in equations (1), (2), and (3), we obtain the following:

$$x + y = ax \tag{4}$$

$$z + y + 4.0304 = b(x + y) \tag{5}$$

$$x + z + 48.000 = cx \tag{6}$$

Substituting in equation (5) the value of z as found from equation (6), we have:

$$(c-1)\,x - bx + (1-b)\,y = 43.9696$$

but according to equation (4) $y = (a-1)\,x$; hence

$$x = \frac{43.9696}{c-1-b+(1-b)(a-1)}$$

The values a, b, and c are all known. a (the quantity of silver chloride obtained from 1 gram of silver) was found by Richards and Wells[48] to be 1.32867; c (the quantity of silver nitrate obtained from the same quantity of silver) was found by Richards and Forbes[60] to be 1.57479. The best results of a present investigation give the value of b as 0.373217. Substituting these values in the equation (7), we obtain x, the atomic weight of silver, = 107.881. Substituting this value in equation (4), we obtain y, the atomic weight of chlorine, = 35.4574, and substituting these values in equation (5) or (6), we obtain z, the atomic weight of nitrogen, = 14.0085.

These three values for the atomic weights of silver, chlorine, and nitrogen are entirely independent of any but the most recent work, and rest directly, through silver nitrate and water, upon the international standard of atomic weights, O = 16.000. It may be noted that if hydrogen is taken as 1.0078 with Noyes, the values of the atomic weights are altered but slightly. Silver becomes 107.879, chlorine 35.456, nitrogen 14.008. The present work thus completes a connected chain of data and furnishes striking evidence in favor of the low values for silver and nitrogen which have recently found support in many other different ways.

It is not without interest, also, to note that if one chooses the old value for silver, 107.93, and for chlorine 35.473, the work just described makes nitrogen = 14.017—a value inconsistent with the value 14.037 calculated from silver nitrate, if silver is assumed as 107.93. Thus the present results are incompatible with the work of Stas, both as regards silver and as regards nitrogen; but they are entirely consistent with the new values of the atomic weights of the elements concerned.

Still more recently I have been engaged with F. B. Coffin and G. S. Tilley, in the Chemical Laboratory of Harvard University, on a similar study of ammonium bromide, the same methods being used. In this case, however, an equal degree of constancy has not as yet been attained. Apparently ammonium bromide has an extraordinary tendency to occlude either ammonia or hydrobromic acid, according as one or the other is in excess at the time of sublimation; and resublimation in a vacuum apparently does not wholly eliminate the impurity. It appears from these results, which have not yet been published and need not be recounted in detail, that 100 parts of ammonium bromide correspond to somewhere between 191.695 and 191.730 parts of silver bromide. This range is far

too wide to furnish important knowledge concerning the ratio in question. From the other work upon nitrogen one would be inclined to expect the value 191.718 parts of silver bromide from 100 parts of ammonium bromide, a quantity between the two extremes just mentioned. There is no reason to believe that the wide range on either side of the expected value was due in any degree to inadequacy on the part of the experimenters; the difficulty seemed rather to lie in the nature of the substance. This investigation, which raises some fear lest the more fortunate work with ammonic chloride gave constant results simply because constant conditions were used throughout, will be continued with the assistance of recent knowledge concerning the hydrolysis of salts of weak bases and the modern theory of indicators; and ammonium chloride also will be further studied in the light of the anomalous results.

LITHIUM AND SILVER.

A far more satisfactory piece of work was the most recent Harvard investigation on atomic weights, a detailed study of the atomic weight of lithium and the composition of lithium perchlorate, carried out with the unusually able assistance of Hobart H. Willard.([71]) This investigation, which is printed in full on the foregoing pages, leaves little to be desired, either from a theoretical or from a practical point of view. Although the details are fully given on pages 3 and 49 of this volume, for the sake of completeness it is worth while to recapitulate in a few words the object and result of the investigation.

The leading idea was the final solution of the problem presented by the atomic weight of silver—an idea which actuated also the preceding investigations concerning sulphur and nitrogen. An entirely new method of attack was adopted in this case, namely, the determination of the quantitative relations of lithium chloride to silver on the one hand and to the oxygen of the corresponding amount of perchlorate on the other hand. It is evident that by dividing one of these ratios by the other the relation of silver to four atoms of oxygen will be obtained. Expressed algebraically:

$$\frac{Ag}{LiCl} \times \frac{LiCl}{LiClO_4 - LiCl} = \frac{Ag}{O_4}$$

Thus the problem resolved itself into discovering just how much silver is needed to precipitate a known weight of lithium chloride on the one hand and how much oxygen must be added to a known weight of lithium chloride in order to convert it wholly into perchlorate on the other hand. The accuracy of the solution of these quantitative problems depended upon the following essentials:

First, the lithium chloride which should serve as the starting-point must be wholly pure—free not only from other metals and non-metals in the form of salts, but also from moisture and from dissolved gases.

Secondly, the amount of silver equivalent to this lithium chloride must be determined by precipitating the chlorine in a known amount of the lithium chloride with such scrupulous care that the end-point might be determined with perfect precision and that the precipitate should carry down with it no traces of either of the two factors in the reaction.

Thirdly, a new sample of this same perfectly pure lithium chloride must be converted into perchlorate in such a way that all of the first substance should be converted into the second without loss, and that the lithium perchlorate which results should be perfectly pure and free from contamination with the solids taken from the vessels during the reaction, from moisture, and from dissolved gases.

These conditions may all be fulfilled within a reasonable limit of accuracy. That is, indeed, the reason why lithium perchlorate was chosen; for lithium perchlorate has the properties needed, and none of the other perchlorates seem to possess them.

In the execution of the program, lithium chloride was fused in a bottling apparatus similar to that already described, but made of fused quartz. At a bright-red heat, hydrochloric-acid gas was passed over the fused mass so that any hydroxide which might have been formed during the earlier part of the dehydration should be converted back into chloride. The gaseous current was then replaced by pure nitrogen until all traces of acid had disappeared from the gas issuing at the end of the tube, after which time the pure, limpid, colorless lithium chloride was cooled and weighed wholly out of contact with moisture. By the methods so often described, with but slight modification, the quantities of silver and of silver chloride exactly equivalent to a given weight of lithium chloride were determined. From these results the atomic weight of lithium was found to be 6.939, nearly 1 per cent lower than the value found by Stas, whose work with this element seems to have been less fortunate than with any other.

Again, similar portions of perfectly pure lithium chloride were treated in flasks of pure fused quartz with a slight excess of perchloric acid. The resulting hydrochloric acid, together with all the moisture, was expelled by air, and the lithium perchlorate after protracted fusion at 300° in dry air was cooled and weighed. The figures may be found in the appropriate part of the full paper; it is enough to say here that since 1 gram of lithium chloride was found to correspond to 2.54455 grams of silver and to 1.50968 grams of oxygen, the atomic weight of silver is $\dfrac{2.54455}{1.50968} \times 64 = 107.871$.

Thus in the last forty years, since 1870, the atomic weights of twenty-eight elements have been investigated in the Chemical Laboratory of Harvard College. The earlier of these investigations were of course less accurate than the later, for many reasons. Lack of time, of proper facilities, and of chemical knowledge all contributed in greater degree to cause imper-

fection in the less recent work than in that more recent; and the author is sure that he could to-day, with the knowledge gained in the intervening time, solve all the older problems more perfectly. He hopes, indeed, to accomplish the repetition of some of the work in the future, without, however, expecting to find any great changes in the figures.

One's confidence in the work can not but be increased by the fact that in spite of the many years which have passed since some of the work was done, not one of all these values has been shown to be seriously in error, and in every case the Harvard value has been accepted by the International Committee on Atomic Weights and by the world at large as more accurate than previous work of others. Yet other researches are now in progress at Harvard University, and it is hoped that the procuring of better conditions in a projected laboratory, to be built especially for this kind of work, will render the application of yet further refinements possible. Great assistance has been generously granted during the last eight years by the Carnegie Institution of Washington in these investigations. Without this pecuniary help the work could not have been carried out on so large a scale; nor could it have attained the same degree of precision.

In the course of these protracted researches, somewhat extended experience concerning causes of error and means of overcoming them has been acquired by the several experimenters. From time to time papers concerning some of the details have been published, but a complete view of this experience can be attained only by reading the original papers. Nevertheless it seems worth while to republish here a brief paper summing up some of the more important points—a paper based upon a series of lectures given in Berlin, especially upon one delivered before the German Chemical Society in 1907. This paper will be found on pages 95–113 of the present volume.

In concluding this account of the Harvard determinations of atomic weights, it is fitting to print a table presenting a summary of all the figures scattered throughout the paper, together with the international table. In the first column are given the names of all the generally recognized elements, and in the second their symbols; in the third column, the international atomic weights are recorded; and in the last column the Harvard values for twenty-eight atomic weights, all reduced to the standard O = 16.000 and Ag = 107.88, are tabulated. It will be observed that only in the cases of antimony and lithium is there any significant difference between the numbers in the third and fourth columns; the former element was studied by Cooke thirty years ago; the latter has been too recently under investigation to have its new value entered in the international table.

Results of the Harvard Investigations on Atomic Weights, together with the Table Presented by the International Committee in 1910.

[Standard, O = 16,000.]

Name.	Symbol.	International atomic weights, 1910.	Harvard atomic weights.	Name.	Symbol.	International atomic weights, 1910.	Harvard atomic weights.
Aluminum.......	Al	27.1	....	Molybdenum.....	Mo	96.0	....
Antimony.......	Sb	120.2	119.9	Neodymium.....	Nd	144.3	144.27
Argon..........	A	39.9	....	Neon..........	Ne	20.0	....
Arsenic.........	As	74.96	74.96	Nickel.........	Ni	58.68	58.68
Barium	Ba	137.37	137.37	Niobium........	Nb=Cb	93.5	....
Beryllium.......	Be=Gl	9.1	....	Nitrogen.......	N	14.01	14.008
Bismuth........	Bi	208.0	....	Osmium........	Os	190.9	....
Boron..........	B	11.0	....	Oxygen........	O	16.000	16.000
Bromine........	Br	79.92	79.916	Palladium......	Pd	106.7	....
Cadmium.......	Cd	112.40	112.42	Phosphorus.....	P	31.0	31.03
Cæsium........	Cs	132.81	132.81	Platinum.......	Pt	195.0	....
Calcium........	Ca	40.09	40.086	Potassium......	K	39.10	39.095
Carbon.........	C	12.00	....	Praseodymium...	Pr	140.6	....
Cerium.........	Ce	140.25	....	Radium........	Ra	226.4	....
Chlorine........	Cl	35.46	35.457	Rhodium........	Rh	102.9	....
Chromium.......	Cr	52.0	52.01	Rubidium.......	Rb	85.45	....
Cobalt..........	Co	58.97	58.97	Ruthenium......	Ru	101.7	....
Columbium.....	Cb=Nb	93.5	....	Samarium......	Sm	150.4	....
Copper.........	Cu	63.57	63.57	Scandium.......	Sc	44.1	....
Dysprosium.....	Dy	162.5	....	Selenium.......	Se	79.2	....
Erbium.........	Er	167.4	....	Silicon........	Si	28.3	....
Europium.......	Eu	152.0	....	Silver...........	Ag	107.88	107.88
Fluorine........	F	19.0	....	Sodium.........	Na	23.00	22.995
Gadolinium.....	Gd	157.3	....	Strontium.......	Sr	87.62	87.621
Gallium.........	Ga	69.9	....	Sulphur.........	S	32.07	32.07
Germanium.....	Ge	72.5	....	Tantalum......	Ta	181.0	....
Glucinum.......	Gl=Be	9.1	....	Tellurium......	Te	127.5	....
Gold...........	Au	197.2	....	Terbium........	Tb	159.2	....
Helium.........	He	4.0	....	Thallium.......	Tl	204.0	....
Hydrogen.......	H	1.008	1.008	Thorium........	Th	232.42	....
Indium.........	In	114.8	....	Thulium.......	Tu	168.5	....
Iodine..........	I	126.92	126.93	Tin............	Sn	119.0	....
Iridium	Ir	193.1	....	Titanium.......	Ti	48.1	....
Iron............	Fe	55.85	55.85	Tungsten........	W	184.0	....
Krypton........	Kr	83.0	....	Uranium........	U	238.5	238.4
Lanthanum.....	La	139.0	....	Vanadium.......	V	51.2	....
Lead...........	Pb	207.10	207.09	Xenon..........	Xe	130.7	....
Lithium........	Li	7.00	6.939	Ytterbium.......	Yb	172.	....
Lutecium	Lu	174.0	....	Yttrium........	Yt	89.0	....
Magnesium......	Mg	24.32	24.32	Zinc...........	Zn	65.37	65.37
Manganese......	Mn	54.93	54.93	Zirconium.......	Zr	90.6	....
Mercury........	Hg	200.0	....				

LIST OF HARVARD PAPERS ON DETERMINATION OF ATOMIC WEIGHTS.

There follows a chronological list of the papers published by Harvard professors bearing upon the subject of the determination of atomic weights. The following abbreviations are used to economize space:

A.Ch.J.=American Chemical Journal (Baltimore, Maryland, U. S. A.).
Ch.N.=Chemical News (London).
E.U.=Experimentelle Untersuchungen über die Atomgewichte, von Theodore William Richards und seinen Mitarbeitern, 1887–1908. Deutsche ausgabe besorgt von J. Koppel (Hamburg und Leipzig, 1909).
J.A.Ch.S.=Journal of the American Chemical Society.
P.A.A.=Proceedings of the American Academy of Arts and Sciences (Boston, Massachusetts, U. S. A.).
Z.an.Ch.=Zeitschrift für anorganische Chemie (Hamburg).
Z.ph.Ch.=Zeitschrift für physikalische Chemie (Leipzig).

Most of the reprints mentioned below (except those in the Chemical News) have been proof-read by the authors.

CHRONOLOGICAL BIBLIOGRAPHY OF THE HARVARD DETERMINATIONS OF ATOMIC WEIGHTS.

1. The relation between the atomic weights of the chemical elements, by Josiah Parsons Cooke. Mem. Am. Acad., N. S., 5, 1 (1854).
2. A revision of the atomic weights of antimony, by J. P. Cooke. P. A. A., 13, 1 (1877).
3. The atomic weight of antimony, by J. P. Cooke. P. A. A., 15, 251 (1880).
4. Atomic weight of cadmium, by Oliver W. Huntington. P. A. A., 17, 28 (1881).
5. A determination of the relation of the atomic weights of copper and silver. First paper, by T. W. Richards. P. A. A., 22, 342 (1887); A. Ch. J., 10, 182 (1888); Ch. N., 58, 68 (1888). E. U. 86.
6. The relative values of the atomic weights of oxygen and hydrogen, by J. P. Cooke and T. W. Richards. P. A. A., 23, 149 (1887), A. Ch. J., 10, 81 (1888); Ch. N., 58, 7, 17, 30 (1888). E. U. 48.
7. Further investigation of the atomic weight of copper, by T. W. Richards. P. A. A., 23, 177 (1887); A. Ch. J., 10, 187 (1888); Ch. N., 58, 55 (1888). E. U. 92.
8. Additional note on the relative values of the atomic weights of oxygen and hydrogen, by J. P. Cooke and T. W. Richards. P. A. A., 23, 182 (1888); A. Ch. J., 10, 191 (1888); Ch. N., 58, 52 (1888). E. U. 80.
9. The analysis of cupric bromide and the atomic weight of copper, by T. W. Richards. P. A. A., 25, 195 (1890); Ch. N., 63, 20, 34, 43 (1891). E. U. 98.
10. A revision of the atomic weight of copper. Fourth paper, by T. W. Richards. P. A. A., 26, 240 (1891); Ch. N., 65, 236, 244, 260, 265, 281, 293, 302 (1892); 66, 7, 20, 29, 47, 57, 74, 82 (1892). Z. an. Ch. 1, 150, 187. E. U. 119.
11. A table of atomic weights, by T. W. Richards. Printed by Harvard University (1892. Revised 1896).
12. On the occlusion of gases by the oxides of metals, by T. W. Richards and E. F. Rogers. P. A. A., 28, 200; Z. an. Ch., 6, 80 (1893); A. Ch. J., 15, 567 (1893). Ch. N., 68, 240, 250 (1893). E. U. 180.
13. A revision of the atomic weight of barium. First paper. Baric bromide, by T. W. Richards. P. A. A., 28, 1 (1893); Z. an. Ch., 6, 441 (1893); Ch. N., 67, 222, 232, 246, 257, 269, 283, 293 (1893). E. U. 224.
14. A revision of the atomic weight of barium. Second paper. Baric chloride, by T. W. Richards. P. A. A., 29, 55 (1893); Z. an. Ch., 6, 89 (1893); Ch. N., 69, 64, 79, 91, 101, 112, 129, 136, 150, 164, 174 (1894). E. U. 255.
15. On the atomic weight of strontium, by T. W. Richards. P. A. A., 30, 369 (1894); Z. an. Ch., 8, 253 (1894); Ch. N., 72, 18, 29, 41, 54, 72 (1895). E. U. 305.
16. On the occlusion of baric chloride by baric sulphate, by T. W. Richards and H. G. Parker. P. A. A., 31, 67 (1894); Z. an. Ch., 8, 413 (1894). E. U. 294.
17. A revision of the atomic weight of zinc, by T. W. Richards and E. F. Rogers. P. A. A., 31, 158 (1895); Z. an. Ch., 10, 1 (1895); Ch. N., 73, 226, 238, 250, 264 (1896). E. U. 331.
18. A revision of the atomic weight of magnesium, by T. W. Richards and H. G. Parker. P. A. A., 32, 53 (1896); Z. an. Ch., 13, 81 (1896); Ch. N., 75, 148, 158, 172, 183 (1897). E. U. 354.

19. A revision of the atomic weight of nickel, by T. W. Richards and A. S. Cushman. P. A. A., **33**, 95 (1897); Z. an. Ch., **16**, 167 (1898); Ch. N., **76**, 284, 293, 307 (1897). E. U. 373.

20. A revision of the atomic weight of cobalt, by T. W. Richards and G. P. Baxter. P. A. A., **33**, 113 (1897); Z. an. Ch., **16**, 362 (1898); Ch. N., **77**, 20, 30 (1898). E. U. 389.

21. A table of atomic weights, by T. W. Richards. P. A. A., **33**, 291 (1898); A. Ch. J., **20**, 543 (1898); Ch. N., **78**, 182, 193 (1898). E. U. 473.

22. On the cause of the retention and release of gases occluded by the oxides of metals, by T. W. Richards. P. A. A., **33**, 399 (1898); A. Ch. J., **20**, 701 (1898); Ch. N., **79**, 19, 27, 42, 52, 68 (1899). E. U. 192.

23. A revision of the atomic weight of nickel. Second paper. The determination of the nickel in nickelous bromide, by T. W. Richards and A. S. Cushman. P. A. A., **34**, 327 (1899); Z. an. Ch., **20**, 352 (1899); Ch. N., **79**, 163, 174, 185 (1899). E. U. 403.

24. A revision of the atomic weight of cobalt. Second paper. The determination of the cobalt in cobaltous bromide, by T. W. Richards and G. P. Baxter. P. A. A., **34**, 351 (1899); Z. an. Ch., **21**, 250 (1899); Ch. N., **79**, 199, 208, 219 (1899). E. U. 427.

25. A revision of the atomic weight of cobalt. Third paper. The analysis of cobaltous chloride and oxide, by T. W. Richards and G. P. Baxter. P. A. A., **35**, 61 (1899); Z. an. Ch., **22**, 221 (1899); Ch. N., **81**, 112, 125, 139 (1900). E. U. 499.

26. A table of atomic weights, by T. W. Richards. P. A. A., **34**, 637 (1899); Ch. N., **81**, 113 (1900).

27. The electrochemical equivalents of copper and silver, by T. W. Richards, E. Collins, and G. W. Heimrod. P. A. A., **35**, 123 (1899); Z. ph. Ch., **32**, 321 (1900). E. U. 498.

28. A revision of the atomic weight of iron. Preliminary paper, by T. W. Richards and G. P Baxter. P. A. A., **35**, 253 (1900); Z. an. Ch., **23**, 245 (1900); Ch. N., **81**, 174 (1900). E. U. 566.

29. Note on a method of standardizing weights, by T. W. Richards. J. A. Ch. S., **22**, 144 (1900); Z. ph. Ch., **33**, 605 (1900).

30. A table of atomic weights, by T. W. Richards. P. A. A., **35**, 621 (1900).

31. International atomic weights, by T. W. Richards. A. Ch. J., **24**, 377 (1900). E. U. 485.

32. The occlusion of magnesic oxalate by calcic oxalate and the solubility of calcic oxalate, by T. W. Richards and C. F. MacCaffrey, and H. Bisbee. P. A. A., **36**, 377 (1901); Z. an. Ch., **28**, 71 (1901).

33. A table of atomic weights, by T. W. Richards. P. A. A., **36**, 544 (1901).

34. The occlusion of hydrogen by metallic cobalt and other metals, by G. P. Baxter. A. Ch. J., **22**, 351 (1899).

35. The standard of atomic weights, by T. W. Richards. P. A. A., **37**, 177 (1901); Z. an. Ch., **28**, 355 (1901). E. U. 492.

36. A new investigation concerning the atomic weight of uranium, by T. W. Richards and B. S. Merigold. P. A. A., **37**, 365 (1902); Z. an. Ch., **31**, 235 (1902); Ch. N., **85**, 177, 186, 201, 207, 222, 229, 249 (1902). E. U. 590.

37. On the accuracy of the improved voltameter, by T. W. Richards and C. W. Heimrod. P. A. A., **37**, 415 (1902); Z. ph. Ch., **41**, 302 (1902). E. U. 527.

38. A table of atomic weights, by T. W. Richards. P. A. A., **37**, 630 (1902).

39. A redetermination of the atomic weight of calcium. Preliminary paper. By T. W. Richards. J. A. Ch. S., **22**, 72 (1900); **24**, 374 (1902); Z. an. Ch., **31**, 271 (1902). E. U. 626.

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Methods Used in Precise Chemical Investigation

BY

THEODORE W. RICHARDS

METHODS USED IN PRECISE CHEMICAL INVESTIGATION.[1]

This paper contains a brief discussion of some of the important precautions common to most accurate researches of a chemical or physico-chemical nature. Many of the details are already well known to expert workers, but they are often not sufficiently heeded; hence a brief recount of them may be of service.

Perhaps before the methods themselves are discussed, a few general remarks concerning the necessity of precise work in modern chemistry may not be out of place. To some the usual methods of preparation and analysis may seem to represent the highest degree of refinement which is really of great usefulness; greater precision may seem to carry with it no important value. For example, how can it help suffering humanity to add another decimal place to an atomic weight? Why should one care to know the exact heat of combustion of a perfectly pure hydrocarbon, when nothing exists in a pure state around us or within us? The common, useful hydrocarbons are in anything but a pure state, even after all the refinement which is necessary before they can serve as a pleasant source of light. Again, why should one spend several years trying to master the determination of the electromotive force of a cell prepared of almost impossibly pure materials, or seek to compare the compressibilities of substances under pressures which are quite beyond the range of ordinary experience?

The essence of the answer to all these questions, which one has a perfect right to ask, was given by Plato more than two thousand years ago, and he probably appropriated the reasoning from Eastern philosophers who preceded him by centuries. I have often quoted this saying, but venture to do so once more. Plato said: "If from any art you take away that which concerns weighing, measuring, and arithmetic, how little is left of that art!"[2] He meant, of course, that the definiteness and precision and soundness of all important conclusions of mankind depend upon the definiteness and certainty of the data upon which they are based, and that definiteness of data is only to be obtained in quantitative fashion. In the light of modern progress one may evidently carry yet further this ancient statement. As

[1] In the following pages there are combined the more important parts of two addresses, namely, that given to the German Chemical Society in Berlin on May 4, 1907, and that given to the American Chemical Society in Cambridge, on December 29, 1909. The former of these addresses is printed in full in the Berichte der deutschen chemischen Gesellschaft, **40**, 2767 (1907). In the present form the paper amounts to a very brief résumé of a series of lectures given at the University of Berlin during the summer of 1907.

[2] Plato, Philebus, § 55 (Jowett's translation, vol. 4, p. 104).

science becomes more scientific, so it becomes more precisely quantitative; in order to draw very subtle conclusions, one must have exceedingly precise data concerning the facts with which the conclusions deal; and the more subtle and complicated the conclusions to be drawn, the more precise must be the knowledge of the facts. Precision is therefore one of the first requisites for scientific advance.

Indiscriminate measurement will lead nowhere, however; the results of the numerical determination of chemical phenomena are by no means all of equal importance. First among all the numerical quantities with which the chemist has to do are undoubtedly the atomic weights. These eighty-odd individual numbers are the most striking and fundamental of the physical records which nature has left us of the creation of the Universe. They are mute witnesses of the first beginnings of the cosmos out of chaos. Whatever view one may take concerning the beginning of all things, this conclusion can hardly be escaped. Investigation of them is one of the first duties of the chemical philosopher who attempts to interpret the world in which he lives. What is the meaning of the periodic system connecting these mysterious numbers? No one who has thought about the matter at all can doubt that a real understanding of the periodic system would take us very far into the understanding of some of the deepest of the unknown laws of the Universe. We have here a cosmic riddle, the answer to which will put into the hands of humanity knowledge heretofore undreamt.

But some may contend that the very exact determination of these quantities is after all an abstract and academic question, not of great practical significance. How will this remote philosophical knowledge yield any practical use? Who can tell? Faraday had no conception of the electric locomotive or the power-plants of Niagara when he performed those crucial experiments with magnets and wires that laid the basis for the modern dynamo. When mankind discovers the fundamental laws underlying any set of phenomena, these phenomena come in much larger measure than before under his control and are applicable for his service. Until we understand the laws, all depends upon chance. Hence, merely from the practical point of view of the progress of humanity, the exact understanding of the laws of nature is one of the most important of all the problems presented to man; and the unknown laws underlying the nature of the elements are obviously among the most fundamental of these laws of nature. In brief, this is the reason why more than twenty years ago the systematic study of the atomic weights was begun at Harvard University by the author. The fact that more accurate data would be of service also to the practical analyst (because this table of eighty elements is perhaps more used than any other table of natural data) was not forgotten; but this consideration was a subordinate one. The really essential consideration was the desire to know more about the nature of material. This idea may be amplified to extend

to all the other properties of material; it is enough here to have demonstrated that the greatest possible precision in one of the most abstract of the questions of chemical philosophy is none too much; and that mankind is really concerned to know the realities which are only to be learned by the most precise experimentation.

But this precise knowledge is not easily attained. As Tyndall said:

Those who are unacquainted with the details of scientific investigation have no idea of the amount of labor expended in the determination of those numbers on which important calculations or inferences depend. They have no idea of the patience shown by a Berzelius in determining atomic weights; by a Regnault in determining coefficients of expansion; or by a Joule in determining the mechanical equivalent of heat. There is a morality brought to bear upon such matters which, in point of severity, is probably without a parallel in any other domain of intellectual action. The desire for anything but the truth must be absolutely annihilated; and to attain perfect accuracy no labour must be shirked, no difficulty ignored.[1]

First among the steps which must be taken in the performance of any accurate piece of chemical or physico-chemical work is the choice of methods to be used, involving the careful study of the nature of the substances which will best serve the purpose in view. Many an otherwise excellent piece of work has been rendered valueless by a wrong choice of material at the beginning; for often no amount of care can obtain significant results from unsuitable substances. On the other hand, a bad method may nullify the use of all one's other painful precautions. As a rule, carefully conducted preliminary experiments are needed to aid in this choice of substance and method, as well as careful study of the literature of the subject. Much of the success of the modern more accurate work upon atomic weights has been due to this careful choice of material and method of approach.

In order to make clearer the importance of careful forethought, it is worth while to emphasize some of the precautions which must be used in choosing the best conditions in a special case, namely, the determination of an atomic weight. Four main requirements face an experimenter approaching an investigation of this kind; these essential conditions must be fulfilled at the outset if the work is to have any value. In the first place, a compound must be selected which may be prepared in a perfectly pure state. Secondly, this compound must contain, besides the element to be studied, only elements with definitely known atomic weights. Thirdly, the condition of valence of the elements in this compound must be definite; the substance must not consist, for example, of a mixture of two stages of oxidation. Fourthly, the compound selected must be capable of exact analysis, or else of exact synthesis from weighed quantities of the elements concerned.

These four requirements are all so obvious that further exemplification of them here is unnecessary. All of them were perfectly clear to Marignac and

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[1] (Tyndall's "Sound," first edition, page 26. See also Jevon's "Principles of Science," I, 380, ed. of 1874.)

Stas, who endeavored always to work in accordance with their demands. Their fulfilment is not, however, always easy, and it often requires wide chemical and physico-chemical knowledge to choose rightly the substance to be studied.

The material and methods having been chosen, the following work naturally resolves itself into two parts; first the qualitative task of the actual preparation of enough pure substance; secondly, the quantitative task of determining its composition, of comparing it with weighed amounts of other pure material, or of measuring some other special property under investigation.

Purity of materials is not always sufficiently sought. Especially physicists are likely to spend infinite pains in measuring some property of a substance so impure that its behavior is not worth a moment's consideration. Even Stas, at times, with all his precautions, did not always attain a reasonably satisfactory result in this respect. Not only inorganic chemists and physicists should strive for purity of materials, however; the methods which are used in the most accurate work are especially applicable also to the products of organic synthesis. The more complicated in structure and the more similar the mixed substances, the more scientific and thorough must be the means used for the preparation of any one of them in a pure state.

The quantitative process, which follows the qualitative purification, may consist either of chemical analysis or of physical measurement. Chemical analysis is of course very different from the qualitative preparation of the material in the circumstance of its fulfilment, although one of the desired results is the same in both cases. In both cases the experimenter wishes to obtain, at the end of his experiment, a perfectly pure substance, uncontaminated by accidental impurities of any kind whatsoever; in so far, the two processes are alike, and the same considerations govern both. The problem of the quantitative determination, however, is vastly increased in difficulty by the fact that not only must the final substance be pure, but also every possible trace of that substance must be produced which can be produced. To use the legal phrase, "the whole truth and nothing but the truth" is sought. In the qualitative purification, 90 per cent of the substance may be lost without any anxiety or concern; but in the quantitative estimation even the thousandth part of 1 per cent must not be lost, if it is possible to prevent its loss; and if a minute percentage is lost, some process must be undertaken to prove its exact magnitude, so that due correction may be made. The extraordinary increase in difficulty imposed by this condition makes the latter problem entirely distinct from the original preparation of pure substance. Physical measurement, whether of density, temperature, pressure, electromotive force, or any other property, is also

of course entirely distinct from qualitative preparation; to it, nevertheless, many of the principles underlying chemical analysis must be applied.

Let us turn first to certain considerations which apply to nearly all chemical work, whether qualitative or quantitative. Several physico-chemical tendencies of matter greatly affect the purity of nearly all preparations. The generality of these tendencies arises from the fact that we usually purify materials of all kinds by changing the state or phase in which it exists. For example, we purify a salt by dissolving and crystallizing it, taking it first into a liquid phase, and then again bringing it back into the solid condition. Again, we purify a liquid by distilling it, a process which of course also involves a double change of phase. Thus the exact purification to be effected by any such process depends in each case upon what happens at the moment of formation of the new phase, as well as upon the completeness with which this phase may be separated mechanically from the residual one.

Evidently the complete separation of the substances concerned depends upon two quite different series of facts. In the first place, the phases must be separated completely from one another; otherwise each will be contaminated with some of the other, which will constitute an impurity. Thus solids must have adhering to them none of the liquid from which they were made, and none must be inclosed in cells within their substance. Liquids must retain none of a finely divided precipitate. Gases must be freed from fine drops or impalpable powder belonging to the phase from which they were to have been separated. This part of the separation is purely a mechanical question. It involves the use of separating methods which depend for their efficiency upon the different properties and characteristics of the phases to be separated.

On the other hand, another more insidious cause of impurity exists, namely, the tendency which every phase has to dissolve something from any phase with which it may come into contact. This tendency manifests itself in solids as the so-called solid solution or isomorphous mixture, in liquids as solubility, and in gases as the vapor tension of the impurity. The contaminating substance retained in this fashion is not merely held in mechanical fashion, but becomes physico-chemically a part of the phase which contains it.

These two causes of contamination both work together to prevent complete separation of one chemical individual from another by any process of purification. Hence their tendencies, different as they are in cause, may be included together under one rule which must always be borne in mind by anyone endeavoring to purify any solid substance. This rule is as follows:

Every substance separating as a new solid phase tends to retain upon itself or within itself some of the other substance in the phase from which it separated.[1]

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[1] Richards, Zeitschr. phys. Chem., **46,** 189 (1903).

This tendency may be very great, as in the case of isomorphous or mutually soluble substances; or very small, as in the case of crystals prepared by sublimation; but the tendency must never be overlooked. Practically it is never safe to assume, without definite proof to the contrary, that a newly produced solid does not contain some of the phase from which it was born.

Hundreds of examples might be cited. Let us consider first the usual ways in which solids formed from liquids may be contaminated. The crudest and most obvious cause of contamination is the purely mechanical one; much liquid adheres to the surface of the solid. In the preparation of pure substances, the centrifugal draining of the crystals is of enormous assistance in eliminating this adhering mother-liquor. The advantages of centrifugal action, which has long been used in technical processes, have found oddly enough but few champions among scientific investigators. Undoubtedly its consistent use for the last fifteen years has contributed much to the success of the Harvard work on atomic weights. The effective separation of mother-liquors is as important in organic chemistry as in the most exact inorganic work; therefore the use of the centrifuge for this purpose may well come to take an important part in all chemical laboratories, whether concerned with organic, inorganic, or physico-chemical problems.[1]

Turning now to a less obvious, but still merely mechanical cause of incomplete separation, one should call attention to the fact that all precipitates or crystals made from aqueous solutions contain included water which does not belong to them, even the beautifully brilliant and apparently quite dry crystals of electrolytic silver.[2] This appears to be very pure, but in reality contains both water and silver nitrate imprisoned in minute cells throughout its structure. Thus, as a rule, every solid prepared from a liquid which is to be weighed with accuracy should be fused in a dry atmosphere before weighing, in order to expel the accidental water. Merely heating, even to 200° or more, is not enough, as the traces of included liquid are not able to force their way out of the firmly knit solid structure.

Water is held, not merely mechanically as in this case, but also in chemical fashion, with great pertinacity. This is well known, and yet the resulting danger to precision is not always sufficiently heeded. Indeed, the unsuspected presence of water is unquestionably one of the most insidious sources of error in any precise chemical work. This omnipresent substance is not easily found by chemical tests, and often produces no important change in the outward appearance of the substance in which it lurks, though its presence may be far more injurious than almost any other impurity.

[1] Richards, Jour. Amer. Chem. Soc., 27, 104 (1905).
[2] Lord Rayleigh and Mrs. Sidgwick, Phil. Trans., 175, 470 (1884). Richards, Proc. Amer. Acad., 23, 177 (1887); Zeitschr. phys. Chem., 37, 336 (1900); also especially Zeitschr. phys. Chem., 46, 189 (1903). Also, Duschak and Hulett, Trans. Am. Electro. Chem. Soc. (1908).

To illustrate the malignant effect of the apparently innocuous impurity, let us consider a specific case. Let us suppose that the atomic weight of nickel is the constant to be determined and that 0.1 per cent of residual crystal water is present in the nickel bromide to be analyzed. This comparatively small amount of impurity would raise the resulting observed value for the atomic weight of nickel 0.22, from 58.71 to 58.93, or more than a third of 1 per cent. The same amount of cobalt bromide present as an impurity would have caused an error only about $\frac{1}{700}$ so great, namely, about 0.0003—an amount wholly negligible. Clearly the elimination of water is one of the most important experimental problems presented to the exact analyst. This has been solved at Harvard by the gradual evolution of a very simple and satisfactory piece of apparatus,[1] which might well find applications in every quantitative laboratory. It consists of an ignition tube fitted into a soft-glass tube which has a projection or pocket in one side. A weighing-bottle is placed at the end of the latter tube, and its stopper in the pocket. The boat containing the substance to be dried is heated in the hard-glass tube, surrounded by an atmosphere consisting of any desired mixture of gases. These gases are displaced, after partial cooling, by pure dry air, and the boat is pushed past the stopper into the weighing-bottle, the stopper being then forced into place and the substance thus shut up in an entirely dry atmosphere. The weighing-bottle may now be removed, placed in an ordinary desiccator, and weighed at leisure. A drawing of the latest form of this apparatus is given on page 24 of this publication.

But the solvent itself is not the only impurity carried down with the precipitate or crystal formed from a liquid; traces of any other substances which may be in solution are also carried down. Thus in any ordinary metathetical precipitation[2] the precipitate is likely to contain traces of all the acids and bases present, besides the elements chiefly constituting the precipitate. Thus silver chloride precipitated from sodium chloride by silver nitrate may contain traces of sodium chloride, of silver nitrate, or of sodium nitrate, according to the manner of its precipitation. The only method of guarding against this source of error is to conduct the precipitation from solutions as dilute as possible. That portion of the substance thus retained which is held or adsorbed only on the surface, may usually be removed by thorough washing; but some is generally imprisoned beneath the surface, and no amount of washing can eliminate this portion.

[1] Richards, Zeitschr. anorg. Chem., **8,** 267 (1895); also Richards and Parker, *ibid.,* **13,** 86 (1897).
[2] See, for example, Richards and Parker, Proc. Amer. Acad., **31,** 67 (1894); Zeitschr. anorg. Chem., **8,** 413 (1895); also Richards, *ibid.,* 23, 383 (1900); also Richards, McCaffrey and Bisbee, *ibid.,* **28,** 71 (1901), etc.

Clearly those precipitates which have a loose, sponge-like structure, such as silver chloride, may be more successfully washed than the rigid crystalline ones; for the innermost pores of the spongy precipitates are accessible, while those of crystalline precipitates are sealed. Hence such precipitates are more suitable for precise work than are crystalline precipitates.

Not only do solids thus formed from liquids tend to hold the impurities which surrounded them at the moment of their formation, but also solids formed from other solids have the same tendency. Thus cupric oxide made by the ignition of the basic nitrate always contains nitrogen gas, which is only eliminated at the temperature at which the oxide begins itself to decompose. Until the prison walls are broken down, the prisoner is unable to escape.[1]

There may be some exceptions to this general rule concerning the inclusion of impurities by solids, but I have never found one. An appreciable part of the cause of the superiority of the most recent determinations of atomic weights over the older work of Stas and his contemporaries may be traced to the careful elimination of this cause of error.

So much for solids: Let us turn now to a more mobile state of matter. The mechanical methods for removing solid impurities from liquids are so well known that attention need not be directed to them here, except, perhaps, to reiterate the advantages of centrifugal treatment and to emphasize in passing the convenience and accuracy of the Gooch-Munroe perforated crucible with a mat of polished platinum sponge.[2] The physico-chemical causes of contamination are less generally known, however. The following rule must always be borne in mind: *All liquids tend to dissolve something from every other phase, solid, liquid, or gas, with which they come in contact.* Sometimes the solubility is so slight as to be negligible; but more often than is generally supposed its extent is appreciable. The vessels in which the operation is conducted are soluble, as well as the precipitate produced within them or the gases above them. Stas, who worked in glass vessels, was never able to free his salts from silica. The plentiful use of vessels of platinum and of fused quartz in modern work has been another reason for the increased accuracy now within reach.

The solubility of precipitates affects the result of final quantitative analysis of the substance in obvious ways. If a precipitate is somewhat soluble in water, it will not all be collected upon the filter, and some means must be taken to estimate the amount which remains in solution. Moreover, if some of the precipitate remains in solution, the end-point of the reaction becomes difficult to detect, for this dissolved portion will be pre-

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[1]Richards, Zeitschr. anorg. Chem., 1, 196 (1892); also Proc. Amer. Acad., 26, 281, (1891); 33, 399 (1898); 38, 200 (1903).

[2]C. E. Munroe, J. analyt. Chem., 2, 241 (1888); Chem. News, 58, 101 (1885). See also Zeitschr. angew. Chem., 14, 923 (1901), and Richards and Staehler, Jour. Amer. Chem. Soc., 29, 633, 1907.

cipitated by either of the ions of which it is constituted. Thus a solution of argentic chloride is precipitated by either a silver salt or a chloride.[1]

In some cases Stas recognized this tendency, especially in his later work; but he did not always sufficiently heed it. The simple instrument which he devised for estimating the traces of precipitate produced by adding suitable reagents to such very dilute solutions has been improved and made more general in its application, receiving the name of "nephelometer" or "cloud-measurer."[2] With this instrument minute traces of suspended precipitate may be approximately estimated from the brightness of the light they reflect. The construction is very simple. Two test tubes, near together and slightly inclined toward one another, are arranged so as to be partly or wholly shielded from a bright source of light by sliding shades. The tubes are observed from above through two thin prisms, which bring their images together and produce an appearance resembling that in the familiar half-shadow apparatus. The unknown quantity of dissolved substance is precipitated as a faint opalescence in one tube by means of suitable reagents; and a known amount, treated in exactly the same way, is prepared in the other. Each precipitate reflects the light; the tubes appear faintly luminous. If, then, the shades have to be adjusted at exactly the same height in order that the precipitates may show like tints to the eye, the precipitates may be assumed to be equal. If, on the other hand, the shade over the standard tube must be arranged so as to expose to the light only half as much of this opalescent mixture as the other shade exposes of the other in order to show a like tint, the former precipitate may be assumed to be about twice as plentiful. Accordingly a new standard tube with a known amount is made, about half as concentrated as before, and a new comparison is made. In this way, in a very short time, the amount of suspended precipitate in the unknown tube may be estimated with considerable precision, and therefore the trace of dissolved substance may be determined.

As is well known, liquids tend to dissolve not only solids, but also gases, as well as other liquids. Thus Stas undoubtedly contaminated his silver with oxygen, by fusing it in an oxidizing environment. His method of suddenly cooling the silver by pouring it into water prevented this oxygen from escaping from the liquid silver in the act of solidifying. The error of 0.05 per cent in his value for the atomic weight of chlorine is to be traced at least in part to this cause, for he assumed that his silver was pure and that the gain in weight on conversion into the chloride represented all the chlorine added.[3] This particular difficulty has only been overcome in recent work through rigorously excluding all oxygen, by fusing silver either in vacuum or in hydrogen.

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[1] Mulder, Silberprobir Methode, 1859; Richards and Wells, Carnegie Institution of Washington Publication 28, page 24, 45 (1905).

[2] Richards, Zeitschr. anorg. Chem., 8, 269 (1895); Richards and Wells, Amer. Chem. Jour., 31, 235 (1904); Richards, ibid, 35, 510 (1906).

[3] Richards and Wells, Carnegie Institution of Washington Publication 28, 2 (1905).

Not only solids and liquids have this tendency of holding back other substances taken from the phases around them, either in a mechanical or physico-chemical fashion; gases also may carry away, both mechanically and physico-chemically, portions of the phases with which they are associated. Everyone knows that gases evolved from solids often carry away fine powder with them, especially where the decomposition of the solid involves considerable molecular rearrangement. It seems as if the molecule in its upheaval is separated from its fellows, and hence an impalpable powder almost of molecular fineness may be carried away with the arising gas. Gases from liquids, also, provided that they escape in the form of bubbles, always carry for a long distance exceedingly fine drops which result from the bursting of these drops on the surface. On the other hand, there is good evidence that the drops are not mechanically carried away to an appreciable extent when the evaporation is conducted without the formation of bubbles, and accordingly quantitative evaporation should be carried out either on the steam-bath or in a vacuum desiccator or with the help of a downward blast of pure air at a temperature just below the boiling-point.[1] The former of these processes can not be used in the most exact work, because it contaminates the substance with the impurity almost inevitably present in the air of the laboratory.

Evaporation or distillation under diminished pressure is especially to be recommended, if carried out with adequate precautions. The considerable lowering of the temperature of the evaporation diminishes the risk of decomposition of a somewhat unstable substance, and greatly decreases the effect of all the solvents and vapors upon the vessels employed. The higher the vacuum, the more advantageous is the process, as a general rule. A moment's thought will show why this should be. If any air still exists in the apparatus the vapor of the liquid to be evaporated may go from the solution to the condenser or to the absorbing material in the desiccator only by pushing aside this air. Passage from the solution to the drying material is then a process of diffusion, which is notoriously slow. On the other hand, if every trace of air is removed, no impediment exists in the passage of the vapor from one place to the other. As the vapor is condensed or absorbed, a partial vacuum is created which is immediately replenished from the liquid to be evaporated, and the process proceeds with great rapidity. Hence a high vacuum is very important in such work, not only because the boiling-point of the liquid is thereby greatly diminished, but also because the transfer of vapor is facilitated.

Physico-chemically, also, gases may carry away impurities by evaporation, as is well known. One must always be on guard against possible loss of material in this way and also against the possible introduction of impurity from incoming gas, which may be contaminated because of aeriform

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[1] For example, Richards and Forbes, Pub. Carnegie Institution of Washington 69, 53 (1907); also the foregoing account of the evaporation of lithium perchlorate, page 39.

impurities taken from so-called purifying agents or improperly used rubber tubes.   For example, it is frequently recommended to purify hydrogen by passing it through potassium permanganate, silver nitrate, strong sulphuric acid, and calcium chloride one after the other.   The potassium permanganate contaminates the hydrogen with traces of oxygen, the silver nitrate is partly reduced by the light of the laboratory and adds an impurity of an oxide of nitrogen, the sulphuric acid fails to remove these impurities and adds sulphur dioxide, because of its own reduction by hydrogen; the calcium chloride, being not so good a drying agent as sulphuric acid, adds water vapor to the other contaminating substances.   Thus the hydrogen emerges from the train of so-called purifiers distinctly less pure than it was in the first place.   Such feats of ignorance are by no means uncommonly recounted in the literature of the subject, and often they have led to the complete nullification of any usefulness which might otherwise have existed in the final results of an investigation.

The construction of the laboratory is by no means unimportant in carrying out precise quantitative work.   The ideal laboratory should be built as the modern hospital is built, and every precaution should be taken against dust and fumes.   Nevertheless, even in a badly arranged laboratory excellent work may be done if precaution is taken to carry out all the manipulations under cover, protected from dust and noxious vapors. Important as the laboratory is, it is by no means the most essential condition of experimentation.   A good chemist can do more accurate work in a poor laboratory than a poor chemist can do in an ideal establishment. No matter how bad the quarters, devices may be used for overcoming the disadvantages of the environment.   Indeed, a good laboratory would be a misfortune if its possession would discourage the use of great precaution at every step of the experimentation.   Other things being equal, however, it is obvious that the best work will be done by the good experimenter when his conditions are as perfect as they can be made; it is certain that bad conditions lessen the output, and by ruffling the temper diminish the value of the work of even the most exact investigator.

Turning now to the quantitative side of the matter, one has to use here measuring apparatus of various kinds.   This apparatus must be good, of course, but extraordinary refinement or outward beauty is not always necessary.   As a rule, physical errors are easier to avoid than chemical ones. This is shown by the fact that physical data are usually known to a much higher degree of percentage accuracy than chemical data.   The difference in precision is by no means due to greater intelligence and care on the one side of the two classes of scientific men than on the other, but rather to the nature of the two problems concerned.

A comparatively simple piece of apparatus whose errors are known and properly allowed for is better than a very complex contrivance whose mechanism is not understood.   Of course, however, in essentials the meas-

uring apparatus must be adequate.   A carpenter can not do good work with dull tools.

The quantitative operation most frequently employed by chemists is that of weighing.   I am often questioned concerning the form of balance fit for work of this kind, usually with the exclamation "What wonderfully fine balances you must have, in order to weigh atoms!"   As a matter of fact, however, any good balance which gives constant results is good enough. The usual errors in weighing arise from the changing buoyancy of the air and the changing hydroscopic and electrical condition of the surface of the vessels weighed; these errors can not be cured by the most expensive and sensitive balance, but must be intelligently eliminated with the greatest care by especial precautions applied to the vessels.   The admirable and important work of Landolt[1] exemplifies this fact in a most striking way. One should always weigh by substitution, using, both as makeweight and as tare, vessels precisely similar in volume, weight, and surface to the vessel containing the substance to be weighed.   The rôle played by the balance itself is nearly always the most accurate part of the whole process, if the weights have been properly standardized.[2]

A word about the scale of operations is perhaps not out of place.   Shall the experimenter use a very large quantity of material, as Stas did, or shall he adopt an infinitesimal quantity as is recommended by Hinrichs?   The answer to this question varies somewhat according to the circumstances of the particular case.   When a small amount of impurity is to be found in a substance, everyone knows that much material should be used in analysis. This is not always so true, on the other hand, when the whole amount of the substance is to be precipitated, instead of merely a very small fraction of it.   When the reaction involves the whole amount of substance, the accuracy of the work depends much more upon the *purity* of the original material and the purity of the precipitate, as well as upon the completeness of the reaction, than upon the quantity of material used in the individual experiments.

For example, Stas used very large quantities of material, sometimes as much as 400 grams of silver in a single experiment, hoping in this way to increase the accuracy of his results.[3]   Obviously, however, since the purely chemical errors, and not the errors of weighing, formed the largest part of the cause of uncertainty in the outcome, this expenditure of time was often misplaced.   To obtain a precision of 1 part in 100,000 it is only necessary to weigh 400 grams to within 4 milligrams.   If the silver contains as much as one-thousandth of 1 per cent impurity there is no use in weighing it more accurately than this.   Now, Stas's silver probably contained at least

[1] Hans Landolt, Sitzungsber, Kgl. preuss. Akad., **15,** 354 (1908); Abhandlungen der Bunsen gesellschaft, No. 1 (1909).
[2] Richards, Jour. Amer. Chem. Soc., **22,** 144 (1900).
[3] Stas, "Untersuchungen," Aronstein's translation, p. 175 (1867).

fifteen times this percentage of impurity. Evidently, then, if he had weighed his 400 grams of silver within 6 centigrams it would have been as accurately weighed as the purity of his material warranted. Ten grams of silver weighed to within a milligram (a degree of accuracy obtainable in any analytical balance) would have brought him just as good results as those which he actually obtained, and 10 grams of silver weighed within one-tenth of a milligram, a result possible on almost any reasonably good balance, would have given him results tenfold as accurate as those which he really obtained, provided that his silver had been pure.

Clearly, then, the enormous expenditure of time put upon these large quantities of materials was time wasted; it would have been much better if he had spent it in making the silver really pure in the first place.

In most of the modern Harvard work upon the subject a greater degree of accuracy than 1 part in 100,000 has not been attempted. Hence, since one-tenth of a milligram of almost any substance is easily seen and easily weighed, ten grams of material is usually enough to use in any experiment. The effort was made, therefore, not to spend needless exertion in preparing enormous quantities, but rather to put time and energy into making the substances which were actually weighed really pure, so that ten grams should consist of nothing but that which it was supposed to be, instead of containing, as Stas's material often did, a milligram or more of subtle and destructive impurity.

Of course it is true that with large quantities, other things being equal, a somewhat higher degree of mechanical accuracy can be attained, but this in many cases is undoubtedly offset by the extraordinary difficulty of preparing a very large amount of any substance in a state of the highest attainable purity.

On the other hand, the use of very small amounts of material in analytical work unquestionably leads to equally great errors from another cause. Here it is easy to purify the substances, but because of the limitations of sight and manual dexterity, it is not possible to analyze them accurately. If only 1 gram of material is taken, for example, one must collect and weigh one's precipitate to within the hundredth of a milligram, in order to attain an accuracy of 1 part in 100,000, and this is practically impossible. Hence, as is so often the case, common sense dictates that the experimenter should usually choose a middle path between the two extremes, using quantities of material not less than 5 grams nor over 50 grams if a degree of accuracy within 1 part in 100,000 is aimed at. With 5 grams this degree of accuracy would be obtained if the weighing is within one-twentieth of a milligram, a degree of precision perfectly possible, as regards both the collecting of the precipitate and the process of weighing.

But the best apparatus and the best methods possess faults, and these faults or deficiencies must be evaluated and corrected before a precise result

is to be obtained. The methods of doing this vary so much with the details of the special processes that nothing but the most general treatment can be attempted here. A general statement of a very important precaution, which should always be borne in mind, may take the following form: In order to eliminate either physical or chemical inaccuracies of observation or method, parallel trials of the type usually called "control experiments" or "blanks" should always be conducted by the same experimenter under precisely the same conditions as those regulating the main experiment.

This principle is indeed often recognized as regards the conduct of ordinary quantitative analysis. It is applied not only in many technical laboratories, but also in most work in pure science. Nevertheless, the principle is not as generally heeded as is desirable. The idea may be extended and used in a great variety of different applications, of which a few examples may be cited.

First let us suppose that a substance is to be evaporated and weighed in a quartz flask. The weighing must be conducted by comparison with a counterpoise flask filled with dry air at the same temperature, cooled in the same fashion as the flask containing the precious material. The weighing must be done by substitution, and during the process of the weighing each flask must be treated in precisely the same way, in order that any errors pertaining to one weight shall pertain equally to the other. Thus in a sense the empty counterpoise flask is a control experiment run simultaneously with the main experiment.

Again, in the quantitative evaporation of a solution the process of evaporation must be tested by repeating it again and again with known amounts of material in order to be sure that none has been vaporized, and none carried away mechanically, as well as to prove that no impurities have crept in from outside during the process. This is illustrated in the foregoing account of the determination of the atomic weights of silver and lithium, when a solution of lithium perchlorate was to be evaporated and weighed.

As a third instance, I may cite the determination of very small amounts of precipitate by means of the nephelometer already mentioned. If one wishes to determine these traces accurately by means of the reflected light sent out from them, one must use as a basis of comparison a tube containing a known amount of the same substance prepared in exactly the same way, every step of the precipitation of the two tubes being identical. In this way accurate results may be obtained; but otherwise great errors may enter, because of differences of solubility caused by changing temperature or the effects of different electrolytes.[1]

Yet another example of quite a different type may be cited. When a thermometer is to be standardized, this standardization should be con-

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[1] Richards, Amer. Chem. Jour., **35,** 510 (1906).

ducted under conditions exactly similar to those in which it is to be used. The same amount of stem must be immersed in the bath whose temperature is to be determined, the same position and method of reading must be employed, etc. In this way the error of reading the thermometer may be eliminated. The standardizing becomes the "blank experiment."

As a final example a new improvement in the determination of specific heats by the method of mixtures may be cited. When a hot body is plunged into a cold calorimeter, or a very cold body is plunged into a warm calorimeter, with the idea of finding the specific heat of the body in question, errors inevitably arise, owing to the necessary proximity of the widely divergent temperatures and the effect of the air through which the body must pass to reach the calorimeter. This has always been a serious difficulty in calorimetry by this method; it has been solved by the application of this principle of running control determinations. The object is very simply attained by repeating the experiment with a hollow shell instead of with a solid body. All the errors which occur in one set of determinations must occur likewise in the other, and they may be eliminated by simple subtraction.[1]

Theoretically, when a method has been perfected and the necessary substances have been purified the course should be plain sailing; but everyone knows that practically this is not the case. If the process has any considerable degree of complexity, so many accidents may happen, so many possibilities of imperfection exist, that it is rarely possible to carry through a long series of experiments without having an occasional failure. Only those unfamiliar with the exigencies of actual work in a laboratory, especially in an imperfectly designed laboratory, would expect anything else. What, now, may be done with these faulty results? Should they be included in the series finally averaged, or should they be rejected? This question is often a perplexing one, but obviously the only method of answering it is to act in such a way that the final results should represent the nearest possible approximation to the truth.

Thus it is clearly foolish to include quixotically experiments freighted with known defects, in computing an average; for experiments containing known defects will certainly not help the investigator to discover the truth. It is equally clear that as a rule all the experiments possessing no known defect should be included in the average, even if they deviate considerably. The only possible exception to this rule might be made in favor of omitting a single experiment from a very long series, an experiment in which the deviation from the average was so far beyond the deviations of all the others

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[1] This method was perhaps first suggested by Pionchon (Compt. Rend., **102**, 675 [1886]). It has been used by N. Stucker (Sitzungst. d. k. Akad. d. Wiss. Wien, May, 1905) and also by W. P. White (Phys. Rev., **26**, p. 536 (1905) to whom I am indebted for the foregoing references. The method has been used quite independently here, without knowledge of the earlier work. See Richards and Jackson: Zeitschr. f. phys. Chem., **70**, 414 (1910).

as to have been obviously due to a mistake in weighing or in reading an instrument. If it can be shown that there is an error equal to that which might be caused by a mistake in reading of a single division on a scale or the omission of a single weight, the presumption in favor of rejecting such an experiment is increased; but even then its rejection is a very doubtful expedient, and the doubtful result should always be given in the table, so that those who would prefer not to reject it may retain it if they desire to do so.[1]

Accordingly it behooves the accurate experimenter to exercise extraordinary precautions as to confirming each weight and each reading of every instrument in order that such lapses may not injure the value of a series of experiments, for whether rejected or not such a mishap inevitably detracts from the value of the series of results. A series from which no experiments have been omitted is always much more satisfactory than one from which it has been necessary to omit individual experiments, even for the best of reasons. The necessity of omitting implies either that the method is liable to accident or that the investigator is too human in his liability to err; and either horn of the dilemma impeaches to some extent the result, even with the bad experiments omitted. If they were not omitted the result would usually be even less satisfactory, however. Of course any omission of experiments simply in order to make an average come out what one thinks it ought to be is wholly outside of the range of conduct of an honest man of science, and it is therefore always essential to state whether any of the experiments have been omitted and the reason, so that the reader may be in a position to judge for himself.

By far the best solution of the difficulty is to discontinue an experiment when anything happens which may introduce error, and not to bring it to completion. Then the average of all the completed experiments represents the nearest approach possible to the truth.

Too much can not be said against the multiplication of incomplete or carelessly obtained data, for such data carry with themselves not only uncertainty and confusion in the present, but also additional labor for the reviser in the future. Every substance must be assumed to be impure, every reaction must be assumed to be incomplete, every method of measurement must be assumed to contain some constant error, until proof to the contrary can be obtained. As little as possible must be taken for granted.

To sum up the matter in a few words, it may be said that the secret of success in a precise chemical or physico-chemical measurement lies in so choosing the particular substance and process and so checking every operation by parallel experiments that both chemical and physical errors may be avoided as effectually as possible; and this choice often involves much study and above all the application of sound common sense. The precautions must be of a consistent order of refinement. Far more depends upon

[1] This recommendation essentially agrees with that made on p. 7 of the new edition of the well-known admirable Ostwald-Luther Handbuch phys. Chem. Messungen (Leipzig, 1910), to which the reader is referred for further suggestions upon many points touched upon here.

this intelligent choice of conditions than upon mere mechanical execution of the operations, although that too is important.

By such painstaking work alone is a precise table of atomic weights or any other table of precise data to be completed.   Are the data worth all the trouble, some of you may ask?   To this I may answer that the fundamental data of chemistry, including the atomic weights, are used continually by thousands of workers throughout the world.   Is it not worth while to provide these countless workers with figures that are somewhere near the truth?   Indeed, an inaccurate table of data is sometimes worse than none, especially if subtle conclusions are to be drawn from them, concerning small differences and divergences.   Moreover, besides the usefulness of the finished data, much new truth is often discovered in the process of attaining the results.   The work throws new light on the physical and chemical properties of the substances concerned, and adds to our experimental knowledge of the behavior of material.   These gains are purely matter of fact, independent of any theory.

Lurking in the recesses of the mind there is always yet another sufficient reason for spending much time on these fundamental figures, namely, the unquenchable curiosity as to what they may mean.   There can be no question that the exact magnitudes of the atomic weights or other physico-chemical constants are intimately connected with the ultimate nature of things.   In natural science, when one wishes to discover the meaning of any fact, he first tries to ascertain as accurately as possible what the fact really is.   The utmost precision is therefore the first step toward the understanding of the ultimate nature of material, with which the atomic weights and all the other physico-chemical constants are so closely concerned.